PB-235 567

A TEST METHOD FOR VOLATILE COMPONENT STRIPPING OF WASTE WATER

Louis J. Thibodeaux

Arkansas University

Prepared for:

Pacific Northwest Environmental Research Laboratory
Office of Water Resources Research

May 1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 235 567

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

W-74-11801

A TEST METHOD FOR VOLATILE COMPONENT STRIPPING OF WASTE WATER,

Thibodeaux, Louis J.

College of Engineering
University of Arkansas
Fayetteville, AR 72701

EPA
Project
R-801876

Environmental Protection Agency, Technology Series, report number EPA-660/2-74-044, May 1974
130p, 27 fig, 9 tab, 21 ref, 3 append.

This work is concerned with the air-strippable volatile organic fraction of industrial wastewaters. The primary purpose was to develop laboratory apparatus and procedures that may be employed to assess the desirability of air-stripping in cooling towers as a treatment operation for removal of a portion of the organics from industrial wastewater. The apparatus developed consists of a short packed (Intalox Saddle) section with liquid recirculation and single pass countercurrent air flow. Desorption is performed in the apparatus at 25°C and ambient pressure conditions.

Desorption experiments were performed on single pure components in water, simulated wastewater preparations and actual industrial wastewater samples. Industrial wastewater samples were representative of: poultry, metal, oil-field, canning, pharmaceutical, paper, food, fibers, petroleum refinery and petrochemical industries. BOD, COD, TOC and gas chromatographic analysis were employed with the experiments.

Industrial wastewaters were found to contain a non-volatile organic fraction that remains in the aqueous phase and a volatile organic fraction that can be transferred to the air phase. Results of one hour desportion runs indicate that the range of the volatile organic fraction is 0% to 70% TOC. The ultimate volatile range was calculated to be 0% to 98% TOC. The volatile organic fractions displayed a range of relative volatilization rates 4.4 to 41.6 times greater than water. The net result of the desorption experiments is that some industrial wastewaters can be effectively treated by air-stripping a sizeable portion of the dissolved organics. (EPA)

Waste Water Treatment, *Cooling Towers*, *Testing Procedures*, *Volatility*, *Industrial Wastes*, Air Pollution, Mass Transfer, Biochemical Oxygen Demand, Chemical Oxygen Demand, Gas Chromatography, Laboratory Tests, Self-Purification, Safety.

Air Stripping, *Desorption*, Industrial Waste Water Treatment, Relative Volatilization Rate, Total Organic Carbon, Intalox Saddle, Volatile Organics, acetone, propanol, methanol, butanol, furfural, phenol, University of Arkansas.

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield VA 22151

05D, 05A

Copy Available from GPO Sup Doc as EP 1.23:660/2-74-044 $ 1.20; microfiche from NTIS as PB $2.25

140

Send To:
WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D.C. 20240

Louis J. Thibodeaux | University of Arkansas

U.S. GOVERNMENT PRINTING OFFICE: 1974— 582—412:42

EPA-660/2-74-044
May 1974

A TEST METHOD FOR VOLATILE COMPONENT STRIPPING OF WASTE WATER

By

Louis J. Thibodeaux
College Of Engineering
University Of Arkansas
Fayetteville, Arkansas 72701

Project No. R–801876
Program Element 1BBO37

Project Officer

John S. Ruppersberger
Pacific Northwest Environmental Research Laboratory
National Environmental Research Center
Corvallis, Oregon 97330

Prepared for
OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office Washington, D.C. 20402 - Price $1.70

ABSTRACT

This work is concerned with the air-strippable volatile organic fraction of industrial wastewaters. The primary purpose was to develop laboratory apparatus and procedures that may be employed to assess the desirability of air-stripping in cooling towers as a treatment operation for removal of a portion of the organics from industrial wastewater. The apparatus developed consists of a short packed (Intalox Saddle) section with liquid recirculation and single pass countercurrent air flow. Desorption is performed in the apparatus at 25°C and ambient pressure conditions.

Desorption experiments were performed on single pure components in water, simulated wastewater preparations and actual industrial wastewater samples. Industrial wastewater samples were representative of: poultry, metal, oil-field, canning, pharmaceutical, paper, food, fibers, petroleum refinery and petrochemical industries. BOD, COD, TOC and gas chromatographic analysis were employed with the experiments.

Industrial wastewaters were found to contain a non-volatile organic fraction that remains in the aqueous phase and a volatile organic fraction that can be transferred to the air phase. Results of one hour desorption runs indicate that the range of the volatile organic fraction is 0% to 70% TOC. The ultimate volatile range was calculated to be 0% to 98% TOC. The volatile organic fractions displayed a range of relative volatilization rates 4.4 to 41.6 times greater than water. The net result of the desorption experiments is that some industrial wastewaters can be effectively treated by air-stripping a sizeable portion of the dissolved organics.

This report was submitted in fulfillment of Project Number R-801876 by the University of Arkansas under the partial sponsorship of the Environmental Protection Agency. Work was completed as of April, 1974.

CONTENTS

		Page
Abstract		ii
List of Figures		iv
List of Tables		vi
Acknowledgments		vii
Sections		
I	Conclusions	1
II	Recommendations	2
III	Introduction	3
IV	Items of Project Study	9
V	Theory of Volatile Component Desorption From An Aqueous Phase	11
VI	Experiment Fabrication, Materials and Methods	22
VII	Experimental Phase and Results	33
VIII	Discussion	63
IX	References	67
X	Publications and Patents	69
XI	Glossary of Symbols	70
XII	Appendices	73

FIGURES

No.		Page
1	Three Major Fractions of Industrial Wastewater	4
2	Schematic of Volatile Desorption Apparatus	14
3	Hypothetical Packed Column Desorption Experiment Results	20
4	Raschig Ring Desorption Apparatus	23
5	Intalox Saddle Desorption Apparatus	26
6	Desorption of Methanol in Water with Raschig Ring Column – COD Analysis	35
7	Desorption of Methanol in Water with Raschig Ring Column – GC Analysis	36
8	Desorption of Acetone in Water with Raschig Ring Column – BOD_5 Analysis	37
9	Desorption of Phenol in Water with Raschig Ring Column – TOC Analysis	38
10	Desorption of Simulated Wastewater No. 1 with Raschig Ring Column	41
11	Desorption of Simulated Wastewater No. 2 with Raschig Ring Column	42
12	Desorption of Simulated Wastewater No. 3 with Raschig Ring Column	43
13	Desorption of n-Butanol with Intalox Saddle Column – Repetitive Runs	44
14	Desorption of Sucrose Solution with Intalox Saddle Column	45
15	Desorption of Poultry Processing Wastewater with Intalox Saddle Column	47
16	Desorption of n-Butanol with Intalox Saddle Column – Interference Tests	48
17	Desorption of Simulated Wastewater No. 4 with Intalox Saddle Column – GC Analysis	49
18	Water Evaporation Calculations in the Raschig Ring Column	51
19	n-Butanol Desorption Calculations with Intalox Saddle Device – Effect of Liquid Rate	52
20	n-Butanol Desorption Calculations with Intalox Saddle Device – Effect of Air Rate	53
21	Desorption Results for Industrial Wastewater Samples – I	58
22	Desorption Results for Industrial Wastewater Samples – II	59
23	Desorption Results for Industrial Wastewater Samples – III	60

No.		Page
24	Relative Volatilization Rates of Industrial Wastewaters	61
25	Petroleum Refinery Wastewater – TOC and GC Experimental Results	62
C–1	The Dow Hollow Fiber Beaker Gas Permeator b/HFG–1	127
C–2	Schematic Diagram of Equipment Arrangement for Gas Permeator Desorption Experiment	128

TABLES

No.		Page
1	Vapor-Liquid Equilibria of Selected Gases and Liquids in Water @ 25°C	12
2	Relative Volatilization Rates and Relative Volatilities @ 25°C – Calculated Results for Eleven Pure Components	16
3	Typical Raw Data From a Desorption Experiment	29
4	Experimental Relative Volatilization Rates for Selected Pure Components with Raschig Ring Desorption Apparatus	34
5	Raschig Ring Experiments Linear Regression Statistical Data for Pure Components	39
6	Air-Volatile Fractions in Industrial Wastewaters	56
7	Published Air-Volatile Fraction Data	57
C–1	Test Results – Volatile Component Desorption in Gas Permeator	129
C–2	Relative Desorption Rates in 1-Hour Run Time	129

ACKNOWLEDGMENTS

The design, construction, and operation of the laboratory units were performed by a team headed by Mr. Jack R. Jones and consisting of Messrs. Charles Cheng, Rick Jones and Mike Gray all of the Department of Chemical Engineering, University of Arkansas. This report was prepared with the assistance of Mrs. Susan Gray.

I wish to acknowledge Drs. J. R. Couper and L. R. Heiple of the College of Engineering and Drs. R. E. Babcock and A. E. Harvey of the Graduate School for their support and encouragement in this project.

The coordination and support provided by Mr. John Ruppersberger (Project Officer) and Mr. Ralph Scott, Environmental Protection Agency, Corvallis, Oregon was greatly appreciated.

SECTION I

CONCLUSIONS

Based on the theoretical and experimental results of this study, it is concluded that:

1. A countercurrent air flow, recirculating liquid, packed stripping column has been developed to perform desorption studies on wastewater samples.

2. The Intalox Saddle Column described on pp.24 and the test method presented on pages 25 and 27 are recommended.

3. This laboratory device can be employed as a laboratory simulation of the air-stripping operation for removal of volatile organics in cooling towers and similar units.

4. This desorption device can be employed as a laboratory test for studies of the volatile character of industrial wastewater.

5. A single desorption study on this device is capable of quantifying the fraction maximum degree of treatment (F_V°) of air-volatile organics in a wastewater sample and the relative rate (K/a) at which the organic fraction can be removed from the water.

6. Nineteen samples of industrial wastewater were desorbed and found to contain an average of F_V° = 33% T O C volatile fraction with a range of F_V° = [0%, 98%].The volatiles in these fractions were 4.4 to 41.6 times more volatile than water.

SECTION II

RECOMMENDATIONS

1. A comprehensive project should be initiated and the desorption apparatus employed to study the volatile character (i.e., F_v^o and K/a) of industrial wastewater. Only nineteen samples were desorbed in this project but the volatile fraction seems to be sizable.

2. The desorbed species should be identified and quantified individually to assess the impact of these components upon the environment.

SECTION III

INTRODUCTION

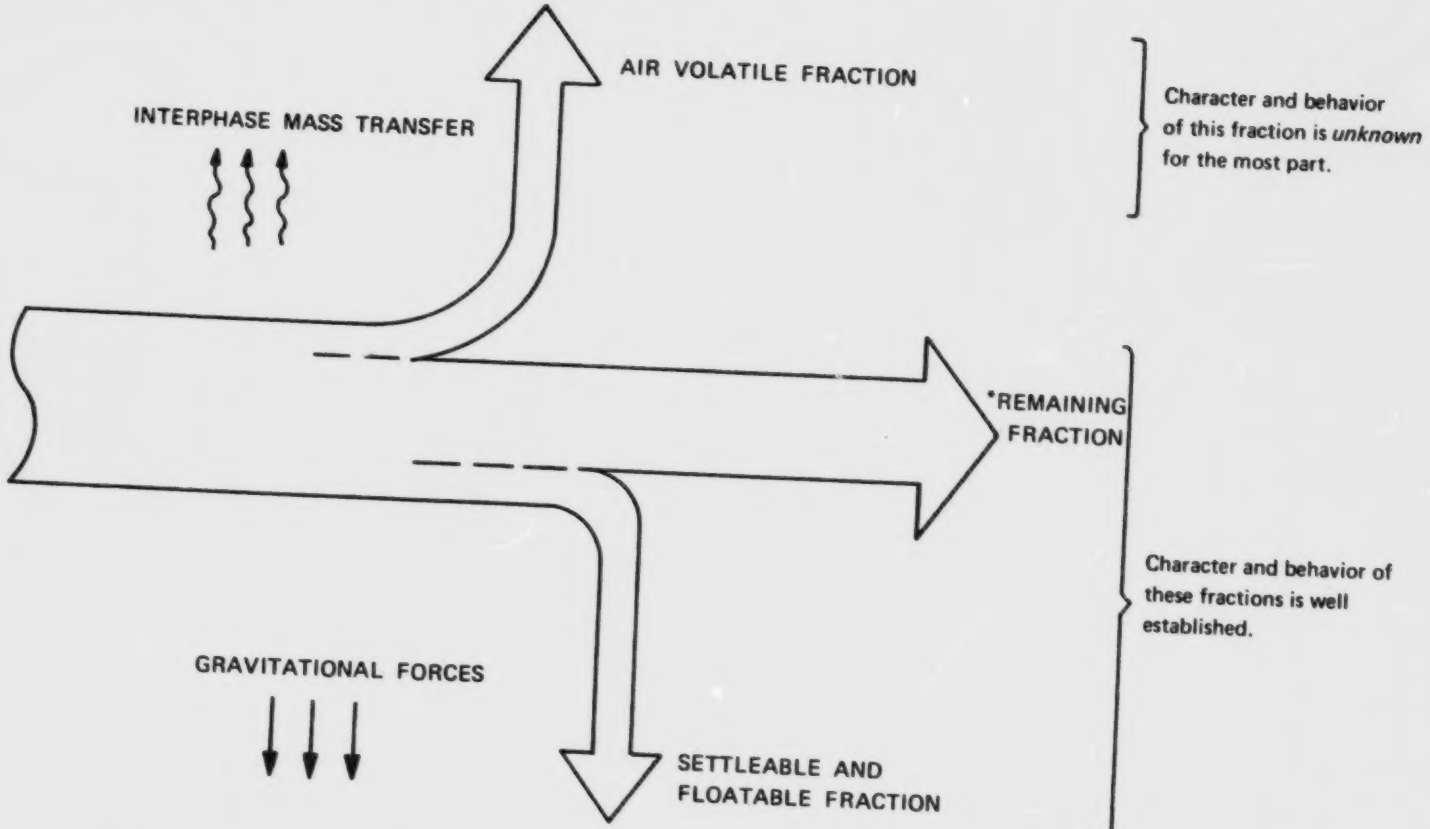
This project is concerned with the development of a laboratory apparatus and experimental procedures for the measurement of the fraction of the dissolved constituents in a wastewater that can be removed by desorbing into air. This research is *not* concerned specifically with the air stripping of ammonia from wastewater. Many industrial wastewaters contain dissolved volatile organics which are easily removed by contact with air, and it is this type of wastewater constituent which this project proposes to study. This project is also concerned with the measurement of the relative ease at which these dissolved, volatile constituents can be transferred to the air phase. The rate of desorption is compared to the rate of evaporation of water. The rate of volatilization of a component must be greater than the evaporation rate of water to effect its removal from water.

All aqueous wastes are immediately acted upon by two ambient physical, natural phenomena which are capable of producing significant changes in the character of the wastewater. These two phenomena are the force of gravity and the chemical potential between phases. The Earth's gravitational force acts upon the differences in density between suspended (solid) particles and water causing some fractions to float to the surface and others to settle to the bottom. The gravitational phenomena effect on wastewater is well known to chemists and engineers. The interphase mass transfer of chemical species caused by a chemical potential between the water and the (ever present) air phase is a more subtle natural phenomena that is invisible and not easily detected by the other senses. Figure 1 is an illustrated representation of the above idea.

The following are some applications to which volatile constituent information can be applied.

Air-Stripping As A Treatment Operation

Quantifying the volatile fraction will place the upper bound on the effectiveness of air stripping as a treatment operation. These operations are typically carried out in a cooling tower type device (induced or forced draft) or in an air sparged (bubble) vessel. The major thrust of this research is volatile organic constituents. Air-stripping has been demonstrated to be a feasible technique for removing a portion of the organics from wastewater. McAlister et al (1) reported 65–85% treatment efficiencies for pulp mill condensates and 40–50% for combined decker filtrates and pulp mill condensates in a cooling tower. These waste streams, in combination with condenser waste from a barometric-type evaporator condenser, are cooled in the tower and reused. Prather (2) reported that an oxidation-aeration cooling tower process offers an economical method of removing small


AIR VOLATILE FRACTION
INTERPHASE MASS TRANSFER
Character and behavior of this fraction is *unknown* for the most part.
*REMAINING FRACTION
Character and behavior of these fractions is well established.
GRAVITATIONAL FORCES
SETTLEABLE AND FLOATABLE FRACTION

*Contains the soluble fraction plus some low volatile and slow settling constituents. This is the fraction that typically receives secondary treatment.

Figure 1. The three major fractions of industrial wastewater.

organic residuals by auto-oxidation and stripping of ammonia and other unwanted gases from refinery wastewater at about the cost of cooling the water. Mohler et al (3) reported experience with reuse and bio-oxidation of refinery wastewater in a cooling tower system. He reported 99.9% efficiencies in removing phenolic-type compounds by bio-oxidation and does not report on the role of air-stripping.

Volatile Losses From Cooling Towers

Information on the volatile fraction in water will aid in the assessment of organic losses during cooling tower operation with recycled process water or wastewater. Once-used water or wastewater can be used as make-up water to a cooling tower. Burns and Eckenfelder (4) report on the adaptation of a cooling tower to improve aeration in an activated sludge plant. A counterflow cooling tower was installed to reduce the influent waste temperature from 120° F to 100° F and to increase the oxygen uptake rate in adjoining aeration tanks. Previous pilot evaluation of plastic trickling filters in series with activated sludge for treatment of pulp and paper waste showed 25% BOD removal in 54 seconds resident times with DOWPAC and 24% BOD removals in 38 seconds with POLYGRID. Cohn and Tonn (5) report on the use of a cooling tower in black liquor evaporation. No reference to organic removal is made but private communications revealed that similar removals as reported by McAlister (1) were being achieved.

Desorption Of Organics During Secondary Treatment

Information on the volatile fraction will aid in the assessment of the magnitude of organic desorption occuring during conventional secondary treatment operations. Gaudy et al (6, 7, 8) performed diffused air-stripping experiments on volatile waste components of petrochemical nature and reported 50% butanone removal in four hours, 50% propionaldehyde in one hour and 50% acetone in 4.5 hours all at 25° C. Eckenfelder (9) reports 20% removal of acetone in four hours in a similar apparatus. The variability of sparged vessel results is due to variations in gas rate/liquid volume ratios. Hiser (10) reported 90% styrene removal in 20 minutes from an aerated flask. He also reported similar total carbon removals from a composite industrial wastewater sample.

Goswami (11) reported that significant removals can occur under quiescent conditions in a batch laboratory vessel. He observed the following removals in twelve hours from a one liter reactor at 25° C; 17.2% removal of acetone, 18% methylethylketone, 27% propionaldehyde, 32.8% butrylaldehyde and 35.3% removal of valeraldehyde.

An analytical simulation model of desorption in aerated stabilization basins by Thibodeaux and Parker (12) indicates that significant removals of selected industrial chemicals are occurring. A study of ten common industrial chemicals in eleven full-scale

aerated basins showed that 20% to 60% removal efficiencies were possible without biochemical oxidation. Detention times ranges from 1.7 to 14.2 days. Laboratory observation of surface agitator desorbers support this data.

Horton et al (13) report the results of a three year study on the changes in tritium content of a large nonseeping outdoor basin. 90% of the tritium contained in an aqueous stream flowing at 15,000 liters per day will be lost to the atmosphere from a shallow basin with a surface area of 6000 m^2. Mackay and Wolkoff (14) derived equations to predict the rate of evaporation of hydrocarbons and chlorinated hydrocarbons (PCBs). These compounds have high rates of evaporation even though the vapor pressure is low. Evaporation "half lives" of minutes and hours is due to the high activity coefficient displayed by these components in aqueous solution.

From the above it appears that a significant amount of volatile components are being stripped and/or desorbed in conventional secondary treatment operations involving the use of air or the presence of large air-water interfaces.

Accumulation Of Volatiles In Enclosures

Information on the volatile fractions in wastewater and their combustible properties may aid in the prediction of potential explosion hazards in closed sewers, manholes, storage vessels, treatment vessels, sumps, etc. Volatile components may accumulate in semi-air tight enclosures and upon combination with air an explosive mixture may result.

Information on the volatile fraction along with data on the maximum safe concentration for breathing will point out potential foul air hazards. It has been the personal experience of the author that the air is quite objectional in some manholes where industrial wastewater is present. Blowers were necessary to remove the foul air prior to entering the manhole.

Wastewater As An Air Pollution Source

Quantifying the volatile fraction will point out and allow one to estimate the importance of species desorption from water as an air pollution source. Most wastewater leaves the process area at an elevated temperature and moves along in an open channel. The two conditions promote rapid desorption of volatile fractions and can be a significant secondary air pollution source. All wastewater treatment operations which involve the contact of air with water (i.e., cooling towers, activated sludge, trickling filters, aerated stabilization basins, anaerobic lagoons, etc.) may also be an air pollutant emission source. Quantifying the volatile fraction in the wastewater will place bounds on this likely air pollution source and show it to be significant or unimportant.

Wastewater As An Odor Source

Information on the volatile fraction in wastewater may pin-point odors emanating from the plant area. Odors can originate from wastewater in the same manner as air pollutants. Hydrogen sulfide is easily desorbed from anaerobic wastewater. The absence of odors from a plant area does not preclude that significant amounts of dissolved gases and liquids are not being desorbed, since many common organics have a high recognition odor threshold in air.

Loss Of Volatiles Effect Wastewater Test Results

Showing the existence of volatiles and quantifying the amount will lead to better sampling and analysis procedures. The loss of the volatile fractions may lead to large errors and widely fluctuating wastewater test results. At present little care is taken to assure that the volatiles do not escape during sampling and handling of industrial wastewater samples in the field or during the analysis in the laboratory. Weimer and Lee (15) reported losses of methane from lake water samples resulted in variable data. Succeeding analysis from the same sample bottle indicated decreasing amounts of methane.

Volatile Losses Effect Wastewater Audits

The proper accounting of all the components (i.e., volatile and non-volatile fractions) will allow more exact material balances and industrial wastewater audits. By-product recovery and accurate design for treatment is based on reliable waste concentration measures. A consciousness of the volatile nature of selected components in the wastewater can lead to better accounting of the waste loads.

Information on the volatile fraction in wastewater, the volatile components, the industry types which are likely to discharge volatiles, and the processes that are likely to produce volatiles, increase our knowledge and understanding of industrial wastewater in general.

Fundamental Desorption Concepts

The volatile character of dissolved constituents in wastewater can be adequately quantified by the experimental determination of two parameters. The symbols and definition of these two parameters and the fundamental concepts revealed by the parameters regarding volatile wastewater constituents are:

Volatile Fraction (F_V°) – this measure denotes the maximum amount (in %) of the original organic pollutants in a water sample that can be removed by air contact.

This is also the maximum efficiency of treatment that can be achieved by stripping the wastewater with air. The organic pollutants in the wastewater can be expressed as BOD_5, COD, TOC and other gross pollutant measures and/or concentration of individual constituents (by gas/liquid chromatography).

Relative Volatilization Rate (K/a) – this measure denotes the ratio of the rate of volatile removal by air contact to the rate water is evaporated in the same apparatus. If the experimental value of K/a is greater than unity, stripping with air may be a feasible treatment operation for this wastewater. If K/a is unity, stripping will have no effect on removing volatile constituents from this wastewater and if K/a is less than unity or zero, stripping will result in an increase of this constituent in the wastewater. This parameter, like F_v°, is dimensionless and both are determined from a single desorption experiment.

SECTION IV

ITEMS OF PROJECT STUDY

The following is a list of the individual items of study considered to be necessary to accomplish the objectives of this project.

A. Develop a laboratory desorption apparatus for a volatile component test method.

1) Test a laboratory bench scale raschig ring packed column as a laboratory desorption apparatus. This column is to consist of a glass tube 5.08 cm. (2 inch) in diameter packed to a height of 45.72 cm. (18 inch) with 0.318 cm (1/8 inch) raschig rings. Air will be introduced at the bottom and liquid into the top. A batch of wastewater will be continuously pumped over the packing. Samples of the liquid taken at predetermined times will be tested for BOD_5, COD, TOC and Gas Chromatograph. The quantity of water lost (weight) will be measured also.

2) Test a laboratory bench scale glass-shot packed column. This column is to consist of a glass tube 2.54 cm. in (1 inch) diameter packed to a height of 20.32 cm. (8 inch) with 0.159 cm. (1/16 in.) glass-shot. This column will be operated just as the raschig ring packed column.

3) Miniaturize and simplify the desorption apparatus. The original apparatus consisted of a packed column, liquid catch basin, pump, and laboratory air. Control and flow measuring means are necessary for the flowing phases. Attempts will be made to devise a method to operate the apparatus (liquid and air movement) with air only. The operation of the apparatus under conditions of natural convection of air and therefore requiring only a liquid pump will be investigated. The lower limit of column size will also be established.

4) Establish the minimum and necessary equipment and apparatus needs. The above column tests, miniaturization and simplification techniques will be aimed at establishing the minimum and necessary equipment, apparatus services, etc. desirable for conducting a reliable volatile component test.

B. Develop laboratory procedures for volatile component test method.

1) Establish the amount of a wastewater aliquot necessary to conduct the volatile test. This volume is charged to the column catch basin and recycled over the packing continuously. Samples for analysis are obtained from the catch basin volume.

2) Establish liquid and gas rates for the apparatus. There is some latitude on the flow rates to the packed section, however, excessive high rates will cause flooding and low rates will prolong the experiment time.

3) Establish the time of test. It is important that the test proceeds long enough that F_v° can be quantified. Tests on a number of components should help establish the

run time that will likely result in the removal of all the volatile constituents.

4) Analysis of experimental data. The raw experimental data will consist of organic concentration (i.e. BOD_5, COD, TOC, G.C., etc.) and water content (grams) with experiment run time (minutes). Analytical expressions have been developed for computing the volatile component parameters from the raw data. Data handling and processing procedures will be developed to compute F_v^o, a, K and K/a. These procedures will be a combination of analytical processes involving algebra and geometry.

C. Apply the proposed desorption test to determine:

1) Which of the several available wastewater test techniques for organic carbon is the most accurate and/or desirable for establishing F_v,
2) Whether or not all the test techniques should result in identical values of F,
3) F_v values for simulated and actual industrial wastewaters,
4) Experimental values of K/a for selected pure components common to industrial wastewaters,
5) Which of the several wastewater test techniques is most accurate and desirable for measuring K/a,
6) K/a values for simulated and actual industrial wastes and selected pure components common to industrial wastewater, and
7) Whether or not all the test techniques should result in identical values of K/a.

D. Other studies important to the volatile desorption test.

1) Compute theoretical K/a for selected pure components. Analytical expressions have been formulated for computing K/a. Theoretical calculations will be related to experimental values.
2) Determine the effect of air temperature and relative humidity upon the K/a measurement.
3) Develop charts and tables by which laboratory measurements of K/a can be corrected to the standard conditions.
4) Decide upon a standard (inlet) air temperature and relative humidity so that all volatile wastewater K/a values can be compared on a common basis.
5) Study possible mass transfer interferences caused by surfactants, inorganic salts, polymers, etc., upon the desorption test results.

SECTION V

THEORY OF VOLATILE COMPONENT DESORPTION

FROM AN AQUEOUS PHASE

Thermodynamic Basis For Desorption

A necessary condition for the transfer of a species from a liquid phase to a gas phase is a favorable chemical potential. The thermodynamic vapor liquid equilibrium of dilute solutions is conveniently expressed by the relative volatility of species A in water:

$$\alpha_{i,w} = \gamma_{i,w} P_i^\circ / P_w^\circ \qquad (1)$$

where $\alpha_{i,w}$ = relative volatility

$\gamma_{i,w}$ = activity coefficient

P_i° = pure component vapor pressure of species i

P_w° = pure component vapor pressure of water

An alternate method of representing this equilibria is Henry's Law:

$$y_i^* = M_{xi} X_i \qquad (2)$$

where y_i^* = mole fraction in the gas (i.e., air) phase for species i

M_{xi} = Henry's Law Constant for species i

X_i = mole fraction in the liquid (i.e., water) phase for species i

The relative volatility reveals more information about the desorbing ability of the species since its removal from water is of main concern here. Table 1 contains a brief summary of relative volatilities and Henry's Law Constant for common industrial gases and liquids. The components 10 through 20 comprise a representative cross section of industrial organic chemicals in wastewater. Many of the common liquid species are more volatile than water and will therefore desorb readily as indicated by a relative volatility greater than unity. Although some high molecular weight organics may have low pure component vapor pressures and high boiling points compared to water they nevertheless exhibit large relative volatilities due to large activity coefficients in water. Pierotti et. al. (16) report activity coefficients of 10^3 to 10^7 for n-acids, n-primary alcohols, sec-alcohols, n-aldehydes, n-ketones, n-esters, n-ethers, n-chlorides, n-paraffins and n-alkyl benzenes.

TABLE 1

Vapor-Liquid Equilibria of Selected Gases and Liquids in Water at 25° C

	Component	Normal Boiling Point, °C	M_{xi}	$\alpha_{i,w}$
1.	Nitrogen	−195.8	86500	2,768,000
2.	Hydrogen Sulfide (H_2S)	− 59.6	54500	1,744,000
3.	Oxygen (O_2)	−183	43800	1,402,000
4.	Ethane (C_2H_6)	− 88.6	30200	966,400
5.	Propylene (C_3H_6)	− 48	5690	182,100
6.	Carbon Dioxide (CO_2)	− 78.5	1640	52,480
7.	Acetylene (C_2H_2)	− 84	1330	42,560
8.	Bromine (Br_2)	− 58.8	73.7	2,358
9.	Ammonia (NH_3)	− 33.4	.843	27.0
10.	Acetaldehyde	20.2	5.88	188
11.	Acetone	56.5	1.99	63.7
12.	iso-propanol	82.5	1.19	38.1
13.	n-propanol	97.8	.471	15.1
14.	Ethanol	78.4	.363	11.6
15.	Methanol	64.7	.300	9.60
16.	n-butanol	117	.182	5.82
17.	Acetic acid	118.1	.0627	2.01
18.	Formic acid	100.8	.0247	.790
19.	Propionic acid	141.1	.0130	.416
20.	Phenol	181.4	.0102	.326

Desorption Of Dilute Aqueous Solutions In A Packed Column

An analytical model of the desorption of dilute solutions of gases and liquids in a packed column has been developed by Thibodeaux, Estridge and Turner (17). The specific volatilization rate for single component i in the desorption apparatus is:

$$K_i = 1 - \frac{(S_{Ri} - 1)}{S_{Ri}\,\mathrm{Exp}[(Z_T/H_{OG,i})(S_{Ri} - 1)] - 1} \qquad (3)$$

where K_i = the specific volatilization rate of species i

S_{Ri} = stripping factor for species i

Z_T = height of the packing, cm.

$H_{OG,i}$ = height of gas phase (overall) transfer unit for species i, cm.

The specific volatilization rate definition is:

$$K_i = (L_{mi}X_{ii} - L_{mo}X_{io})/L_{mi}X_{ii} \qquad (4)$$

where L_{mi} = molar liquid flow rate into packed section, moles/time • area

L_{mo} = molar liquid flow rate out of packed section, moles/time • area

X_{ii} = concentration of species i entering packed section, mole fraction

X_{io} = concentration of species i leaving packed section, mole fraction

The stripping factor definition is:

$$S_{Ri} \equiv M_{xi}\,Gm/Lm \qquad (5)$$

where Gm = molar gas flow rate in packed section, moles/time • area

From equation (3) it is evident that K_i and hence the fraction of species i removed in a packed section (Figure 2) is dependent on Henry's Law Constant, gas flow, liquid flow, height of packed section, and the efficiency of the packing (i.e., $H_{OG,i}$) but not on the concentration of species i in the liquid. Assumptions necessary for use of equation (3) are that the operation be isothermal, steady countercurrent flow, inlet air contains no species i, and concentration of species i in water is very dilute (i.e., $X_i \ll 1$).

The derivation of equation (3) assumes that the liquid concentration in the packed section changes from top to bottom. Removal of this last assumption results in a simpler equation:

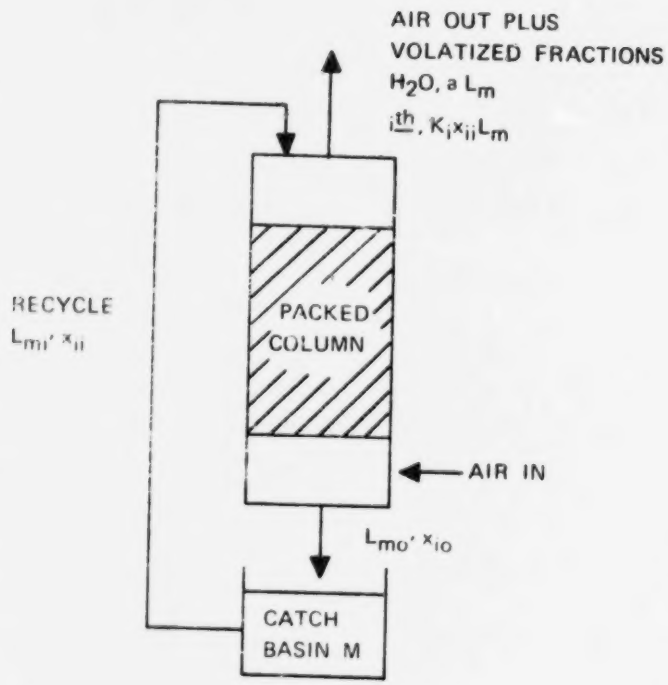


Figure 2. Schematic of volatile desorption apparatus.

$$\hat{K}_i \simeq S_{Ri} [1 - 1/EXP(Z_T/H_{OG,i})] \quad (6)$$

This development is exact for water evaporation

$$a = S_{Rw}[1 - 1/EXP(Z_T/H_{OG,w})] \quad (7)$$

where a = fraction of water lost in column.

Water is most abundant in wastewater and changes little in concentration in the packed section.

If the quotient K_i/a (defined as the relative volatilization rate) is created from equations (5), (6) and (7) and $Z_T \to \infty$ the thermodynamic relative volatility results:

$$\alpha_{i,w} = \frac{S_{Ri}}{S_{Rw}} = \frac{M_{xi}}{M_{xw}} = \lim_{Z_T \to \infty} (K_i/a) \quad (8)$$

This limit is immediate in the case of equations (6) and (7) but a numerical proof was necessary in the case of equations (5) and (7). Calculations were performed with a 3 cm. x 15 cm. Intalox packed desorption apparatus to compare K/a using the exact equations (5, 7), the simplified equations (6, 7) and the relative volatility (8). Data for computing height of a transfer unit for the packing (i.e., $H_{OG,i}$) was from Treybal (18). Table 2 shows the calculated results for eleven common industrial chemicals. The simplified equation values of K_i/a 's less than $\alpha_{i,w}$ as expected. Roughly correlated the relative volatility is related to K/a by:

$$\alpha_{i,w} = (1.032 \pm .108) \times (K_i/a) \quad (9)$$

This estimating equation will yield low values of $\alpha_{i,w}$ for highly volatile components, however this result shows K_i/a is closely related to the actual relative volatility of the pure components.

Most wastewaters contain several dissolved species. The above development is for single species only. Desorption occurs simultaneously for each species and equations (5) and (7) remains valid in a multicomponent mixture provided no synergystic effects are present. Whereas K and a are highly dependent on the operating characteristics of the desorption apparatus, the parameter K/a is somewhat insensitive to actual operating characteristics. Equation (8) indicates that the experimental K/a values for pure components or mixtures can be a useful parameter to quantify the volatility of constituents dissolved in wastewaters.

TABLE 2

Relative Volatilization Rates and Relative Volatility @ 25°C

(calculated results)

Component	$H_{OG,i}$[1]	$\alpha_{i,w}$	K_i/a[3]	$\hat{K}_i/a$[4]	Error[2]
Acetaldehyde	38.7 (cm.)	188.	159.	169.	+6.3
Acetone	35.8	64.1	60.0	61.4	+2.3
Isopropanol	35.4	37.8	36.4	36.9	+1.4
Normal Propanol	34.7	15.1	14.8	14.9	+ .7
Ethanol	34.4	11.6	11.4	11.5	+ .9
Methanol	34.3	9.58	9.49	9.52	< .5
Normal Butanol	34.2	5.82	5.77	5.78	< .5
Acetic Acid	34.1	2.00	2.00	2.00	.0
Formic Acid	34.0	.789	.788	.789	.0
Propionic Acid	34.0	.416	.415	.415	.0
Phenol	34.0	.326	.326	.326	.0

1 – Z_T = 15 cm.

2 – Error of $\hat{K}_i/a$ wrt K_i/a , percent

3 – Exact value

4 – Simplified equation value

Experimental and Data Interpretation Model for Packed Column

A desorption apparatus consisting of a packed column was the only device employed in this work. Desorption apparati consisting of packed towers and sparged vessels were employed by McAlister, Turner and Estridge (1). It was discovered early in the above research that excessive foaming made sparged vessel desorption unpractical for pulp and paper waste. It has been the authors experience that the sparged vessel also requires longer experiment times than the packed column. Both types of desorption apparatus employ a batch of liquid and therefore the behavior of each is transient in nature. The batch-sparged vessel is doubly transient in nature because the interfacial area for mass-transfer is dependent on the quantity of water remaining and water is readily vaporized in this apparatus.

The schematic of the packed column desorption apparatus shown in Figure 2 is helpful in visualizing the mathematic model of the packed column desorption experiment. A volume of sample is charged to the catch basin and pumped around and recycled over the packing continuously. The model further assumes a constant air rate containing no volatiles, constant wet bulb temperature, constant operating temperature and that the quantity of volatiles removed is a constant multiple of the quantity of this component entering the tower (i.e., molar desorption rate = $K_i X_i L_{mi}$).

A differential component balance for water and species i yields two simultaneous equations (17). If the concentration of water is much greater than the concentration of species i (i.e., $X_{H_2O} >>> X_i$) an analytical solution is immediate:

$$\log X_{it} = \log X_{io} - (K_i/a - 1) \log [M_o/M_t] \qquad (10)$$

where X_{it} = concentration of species i in the desorption apparatus at sample time, t, mg/l.

X_{io} = concentration of species i in the desorption apparatus at start of experiment, mg/l.

M_t = quantity of water in the desorption apparatus at sample time t, grams.

M_o = quantity of water in the desorption apparatus at start of experiment, grams.

A log-log graph of concentration of species i, X_{it}, and the quantity of water remaining, M_t, results in a straight line with slope equal to $(K_i/a-1)$. A single desorption experiment thus yields a value of the relative volatilization rate. Equation (10) shows that as water is lost the concentration of species i decreases for $K_i/a > 1$, remains constant for $K_i/a = 1$ and increases

for $K_i/a < 1$. Water is vaporized at a constant rate and is related to run time:

$$M_t = M_o - a\, L_m\, t \tag{11}$$

where t = run time in minutes.

This relation must be used to compute a.

Industrial wastewaters may contain dissolved species of different relative volatilities. Some dissolved components may be more volatile than water and others may be less volatile than water. Gross organic pollutant measures (i.e., BOD_5, COD, TOC, etc.) quantify the concentrations of the combined volatile and non-volatile components. Gross concentration measures can be expressed as the sum of the concentrations of the volatile and non-volatile portions:

$$C^\circ = C_v^\circ + C_{nv}^\circ \tag{12}$$

where C° = the concentration of organic pollutants as measured by the BOD_5, COD, TOC tests, etc., mgO_2/l, mgC/l.

C_v° = the concentration of organic pollutants which are more volatile than water, mgO_2/l, mgC/l.

C_{nv}° = the concentration of organic pollutants which are less or of equal volatility of water, mgO_2/l, mgC/l.

A single desorption experiment on a sample of wastewater will yield C_v° and the relative volatilization rate of the dissolved volatiles.

A detailed theoretical development for desorption operations involving multicomponents is presented by Thibodeaux, Estridge and Turner (17). The following is a brief summary of the working relationships needed for data analysis associated with the desorption apparatus.

The relationship of the volatile and non-volatile fractions in a wastewater consisting of m non-volatile components and n volatile components is:

$$F_t = \sum_{i=1}^{n} F_i^\circ [M_t/M_o]^{K_i/a} + \sum_{j=1}^{m} F_j^\circ \tag{13}$$

where F_t = the fraction of the total amount of the gross constituents remaining in the wastewater at time t ($F_t \equiv C_t M_t / C^\circ M_o$).

F_i° = the original fraction of volatile component i in the wastewater ($F_i^\circ \equiv X_{io}/C^\circ$).

F_j° = the original fraction of non-volatile component j in the wastewater ($F_j^\circ \equiv X_{jo}/C^\circ$).

This equation shows that as run time proceeds and water is vaporized (i.e., $M_t \rightarrow O$) the non-volatile fraction remains. Although a gross concentration measure cannot single out individual constituents, a slight change in the form of equation (13) allows further study of the volatile fraction. If the volatile fraction is assumed to be made of a single "pseudo volatile component" then equation (13) can be reinterpreted as

$$F_t = F_v^\circ [M_t/M_o]^{K_s/a} + F_{nv}^\circ \qquad (14)$$

where F_v° = the original fraction of all the volatile components in the wastewater ($F_v^\circ \equiv C_v^\circ/C^\circ$).

F_{nv}° = the original fraction of all the non-volatile components in the wastewater ($F_{nv}^\circ \equiv C_{nv}^\circ/C^\circ$).

K_s = the relative volatilization rate representative of all the volatile components in the wastewater.

The "pseudo volatile component" is a fictitious lumped single component with a relative volatilization rate of K_s/a which is equivalent, in gross combined behavior, to the n volatile components with individual K_i/a 's. Figure 3 shows calculated results of the behavior of the organic fraction, F_t, for various hypothetical relative volatility values, as a function of the fraction of water remaining. This hypothetical wastewater has a volatile organic fraction of 80%.

Now, if only the volatile fraction is considered, equation (14) may be transformed to yield

$$\log \phi_t = (K_s/a) \log [M_o/M_t] \qquad (15)$$

where $\phi_t \equiv (F_t - F_{nv}^\circ)/F_v^\circ$ is the fraction of the original volatile fraction remaining at run time t.

A log-log plot ϕ_t vs $[M_o/M_t]$experimental data yields information about K_s/a. Reinhardt (19) has demonstrated that K_s/a is not constant if the wastewater contains several components with different relative volatilities. By the use of a graphical interpretation technique, as shown in Figure 3, and equation (15) it is theoretically possible to establish

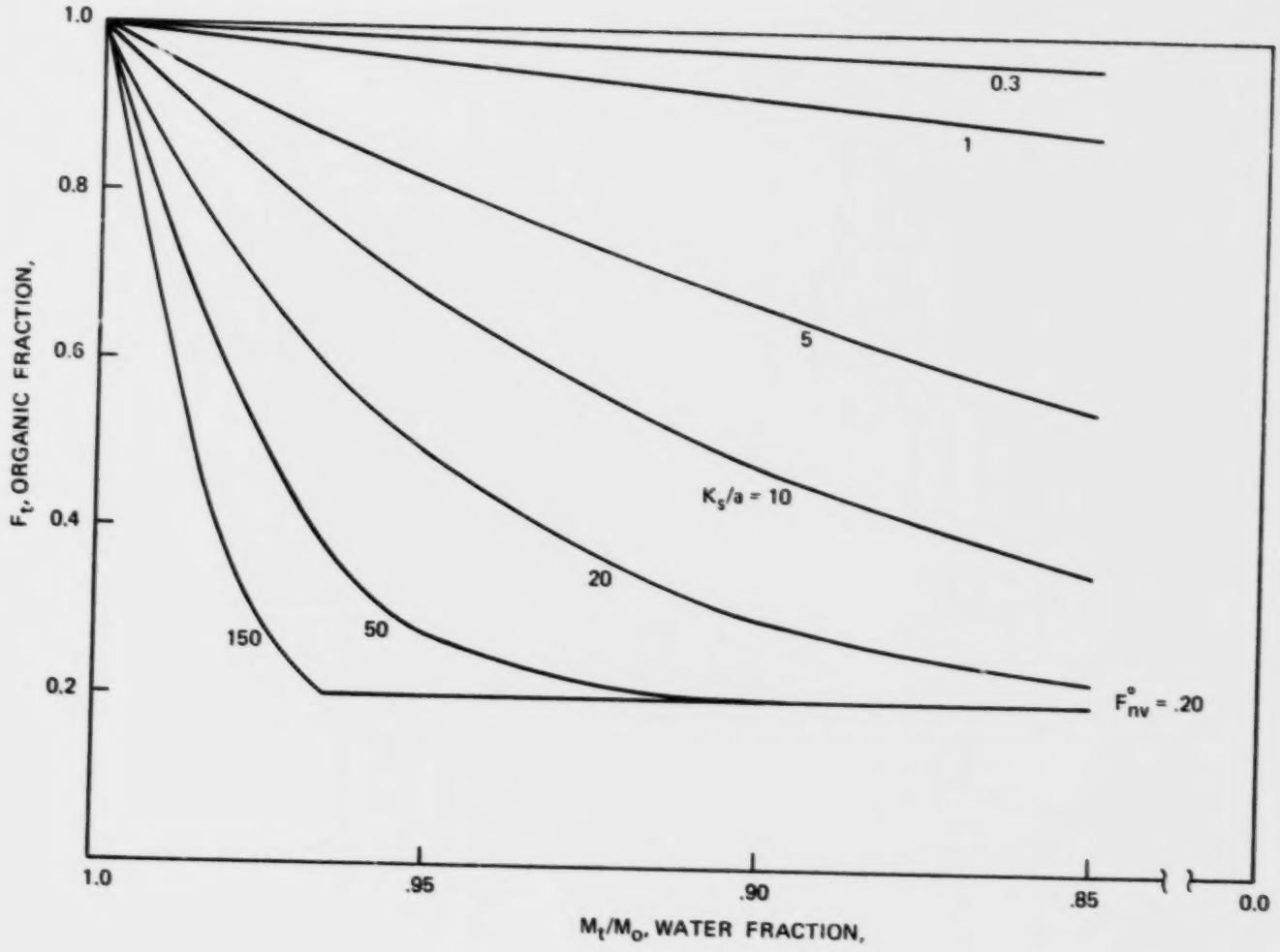


Figure 3. Hypothetical packed column desorption experiment results.

the volatile and non-volatile organic concentrations and an estimate of the relative volatilization rate by a single packed column desorption experiment on a sample of wastewater.

SECTION VI

EXPERIMENT FABRICATION, MATERIALS AND METHODS

Packed Column Volatile Component Desorption Apparatus

Initial packed column desorption studies were performed by McAlister, Turner and Estridge (1). The column employed was of pilot scale dimensions. It was a square columnar gas-liquid contactor of 232 square cm. (0.25 square ft.) cross-sectional area and Plexiglas construction. Overall height was approximately 3.66 meters (12 feet), 3.05 meters (10 feet) of which were packed with Poly-Grid media stacked vertically on 2.86 cm. (1 1/8 inch) centers. The experimental work performed on this pilot scale tower gave excellent desorption results and was an aid in predicting the effect of air stripping as a wastewater treatment operation.

The above described tower was much too large to be practical as a routine laboratory test apparatus for desorption studies. As has been pointed out previously a packed column desorption device has been demonstrated to be the best possible desorption apparatus from an operational point-of-view. Two laboratory or bench scale, packed column desorption devices were employed in the present study.

Raschig Ring Column Desorption Apparatus

A schematic of this apparatus is shown in Figure 4. The apparatus was bench scale and was placed in a standard laboratory hood enclosure.

Glass tubing was used as the column shell. The inside diameter was 4.76 cm. (1 7/8 inches) and the wall thickness was .318 cm. (1/8 inch). The length of the column was .914 m. (3 feet) with a bed support 15.24 cm. (6 inches) from the bottom of the tube. The bottom 15.24 cm. (6 inches) of the tube was graduated in inch marks. The bed support was a circular piece of stainless steel wire screen which rested upon glass knobs on the inside of the tube wall. Ceramic Raschig rings, 1.27 cm. (1/2 inch) size, were used as the packing material; the rings were placed on top of the bed support to a height of .610 m. (2.0 feet). A clearance of 15.24 cm. (6 inches) remained above the top of the packing. The column was secured in a vertical position with the aid of a bubble level.

A four liter glass beaker was used as the solution catch basin. The bottom of the column was elevated above the counter top so that the beaker could be positioned underneath. The beaker was adjusted so that the bottom of the column was submerged in the solution held by the beaker. This offered a liquid seal for the bottom of the column. This seal could only withstand a pressure of approximately 15.24 cm. (6 inches) of water. Tygon tubing and a variable speed pump were used to pump the liquid from the catch basin

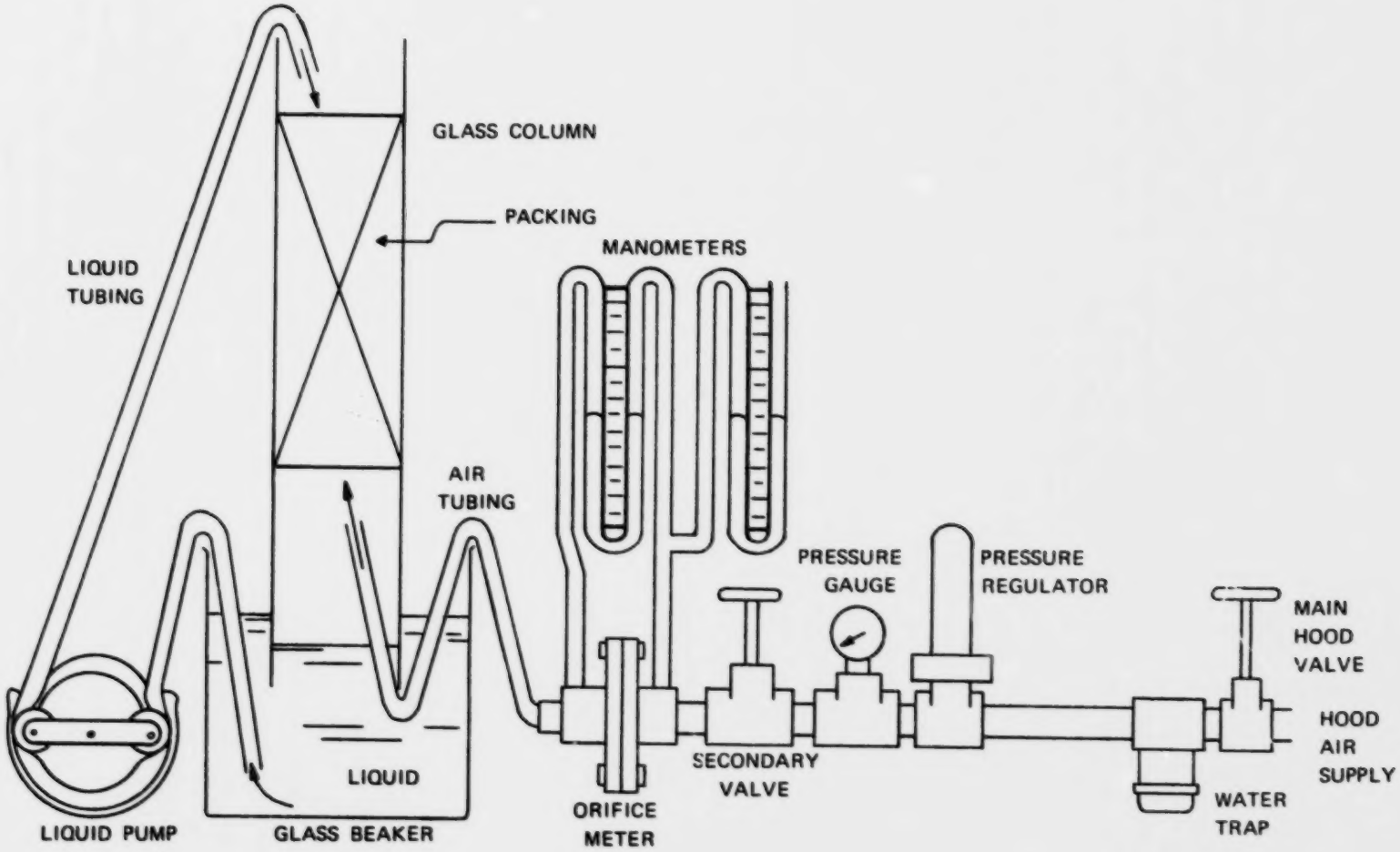


Figure 4. Raschig ring desorption apparatus

to the top of the column. The solution was allowed to exit from the Tygon tubing and fall approximately 2.54 cm. (1 inch) to the top of the packing. From the top of the packing, the solution sought its own path down through the packing, finally, into the catch basin. A thermometer placed in the catch basin measured the temperature of the solution.

The countercurrent flowing desorption gas used was compressed air which was obtained from an air outlet within the hood. Before entering the column the air passed through the following devices: a water trap; a drying agent (DRIERITE) to remove water vapor; a pressure regulator; a pressure gauge; a valve; and an orifice plate (.254 cm. = 1/10 inch). The orifice differential pressure was measured with mercury manometers. From the orifice outlet, the air traveled through Tygon tubing which ended inside the tower about 1.27 cm. (1/2 inch) beneath the wire screen support. A thermometer placed in the air line after the orifice meter measured the dry bulb temperature of the entering air.

Solution samples from the catch basin were withdrawn with a volumetric pipette. The samples were placed in rubber stoppered test tubes and stored in a refrigerator at ~35°F (~2°C) until time for analysis. A low temperature is needed to minimize loss of volatiles during sample storage.

Operating conditions:

Solution or wastewater volume placed in catch basin beaker = 2 1/2 to 3 liters.

Solution flow rate = 700 ml./min.

Air flow rate = 52.8 l. at STP/min. (1.83 SCF/min.).

Pressure at column outlet was ambient atmospheric.

The quantity of water lost by evaporation was obtained by initial and final weight of water in the catch basin beaker with allowances made for water retained in tubing, packing and column.

15 ml. samples were obtained from the beaker every 15 minutes for a period of 3 1/4 hours (14 samples total).

Intalox Saddle Column Desorption Apparatus

Experience obtained with the above device led to the fabrication of a still smaller column desorption apparatus. An illustration of this device is shown in Figure 5. Three models were attempted before this one was decided upon. Glass shot packing proved to be inadequate at the high gas/liquid ratios desirable for a short experiment time.

The column consisted of a male ground glass joint (~20 cm.) topped with a glass funnel with a 10 cm. (large) opening. The internal diameter of the column was 3 cm. and a stainless steel screen, supported on glass indentures, was placed near the bottom but above the ground glass joint. The column was packed to a height of 15 cm. with .953 cm. (3/8 inch) Intalox saddles. The top inlet nipple was fitted with a sample aperature (see illustration). The catch basin consisted of a erlenmeyer flask (500 ml.) fitted with a ground glass female joint. An air inlet nipple and liquid outlet nipple completed the desorption apparatus. The

relative positions of the nipples is shown in Figure 5.

Auxiliary equipment necessary to operate the apparatus consisted of a parastaltic pump (threaded tubing type with removable pump heads), magnetic stirrer and hot-plate combination, bottled dry air and pressure regulator. Interconnecting tubing was Tygon. Consult Figure 5 for arrangement of the pieces of equipment. A thermometer (Hg type) placed in the funnel opening under the downspout measured the liquid temperature.

Operating conditions and procedure:

Assure apparatus is clean and dry and contains the required quantity of packing in the joint and the stirrer bar in erlenmeyer flask. Assemble modified joint and erlenmeyer flask as shown in Figure 5.

1. Calibrate parastaltic pump with plastic tubing (Tygon or equivalent) and set flow rate at about 150 ml./min. with tap water (130 to 160 ml/min. range).
2. Connect a .9 – 1.2 m. (3 – 4 ft.) length of this tubing to bottom nipple on erlenmeyer and nipple on joint.
3. Add 300 to 350 ml. of wastewater to the apparatus through the funnel opening. The sample added should contain a minimum of floating, suspended or settleable solids. Record the exact quantity of sample added.
4. Weigh assembled apparatus, attached tubing and wastewater as a single unit. Record this initial weight.
5. Thread the recycle tubing through the parastaltic type (squeeze) pump.
6. Connect dry, oil free laboratory (or bottled) air to the top nipple of the erlenmeyer with rubber tubing.
7. Adjust apparatus and contents to 25°C.
8. Start magnetic stirrer and adjust pump to deliver water to packing at preset (150 ml./min.) rate. Maintain this liquid rate (130 – 160 ml./min.) throughout the experiment.
9. Upon starting pump take an initial sample (1 ml.) immediately. Carefully record the quantity of sample withdrawn and the time.
10. Immediately after starting pump adjust and maintain air flow rate so that flooding is incipient (~ 12.1 l./min. at STP). Maintain this air flow rate throughout the experiment. Flooding is an undesirable phenomena in countercurrent packed columns that is characterized by excessive liquid hold-up in the packing, so that the gas begins to bubble through the liquid and eject liquid droplets out the top of the apparatus.
11. Operate in this fashion for a period of one to three hours. Withdraw and record volume of samples (usually 1 ml.) at convenient time intervals (5 – 10 min.). Adjust the temperature of the liquid to 25°C ± 1°C by means of hot plate or heating tape placed around the base of the erlenmeyer. The entering dry air will cause the water in the apparatus to cool significantly

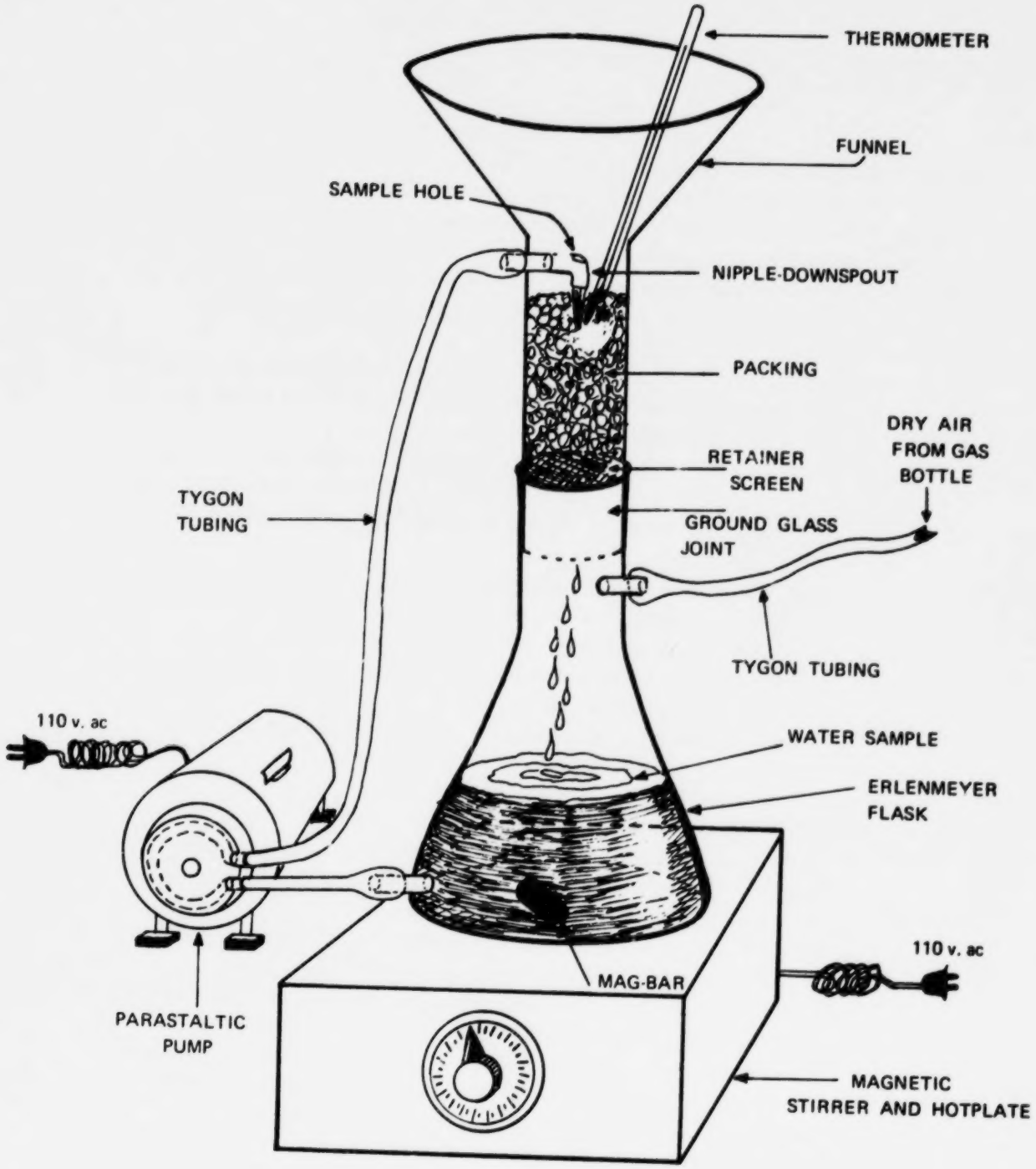


Figure 5. Intalox Saddle desorption apparatus

due to the evaporative loss of water. Heating will be necessary to maintain a 25°C operating temperature.

12. Upon completion of the experiment stop the air flow, shut down the pump and turn the heater off. Record the final run time.
13. Withdraw the final sample.
14. Disconnect the air tubing from erlenmeyer and unthread the liquid tubing from the pump.
15. Re-weigh the assembled apparatus, attached tubing and remaining wastewater as a single unit. Record this weight.
16. Disassemble apparatus and clean parts in preparation for next run.
17. Keep samples under refrigeration (~35°F = 2°C).

Wastewater Test Methods

Samples obtained from the desorption apparati were analyzed for their organic concentration. Analysis performed were: 5 day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), gas chromatograph (GC) and total organic carbon (TOC).

For the BOD_5 and COD tests, the apparatus and procedures described in *Standard Methods* (20) was employed. For the GC analysis a Perkin Elmer Model 800 equipped with 1.83 m. (6 foot), .318 cm. (1/8 inch) O.D. columns was used. Separation columns used were:

amine and K-400 on 35 mesh size particles

15% Chrom-W on 80 – 100 mesh size particles

The flame ionization unit on the chromatograph was used exclusively with a Speedmatic G recorder. One microliter to ten microliter samples were employed.

TOC analysis were performed by instrument also. An Oceanographic International Model 0524 (ampule type) was employed for the bulk of the experimental work. A Beckman Model 915 (injection type) Total Organic Carbon Analyzer was used on samples from eight desorption experiments.

A single inorganic desorption experiment was performed with ammonia. *Standard Methods* (20) was employed in the ammonia analysis.

Experimental Data Handling Techniques

The raw data obtained from the desorption experiment consisted of:

a) independent variable time (t) in minutes
b) dependent variable water content (M_t) in grams and
c) dependent variable organic concentration (C_t°) in mgO_2/l, mgC/l, or area units/l.

The water content at each time is proportional to the run time and the total quantity of water vaporized during the run. The total quantity of water vaporized is computed by:

$$\Delta M_T = W_i - W_f + n \bullet \Delta m \qquad (16)$$

where ΔM_T = total mass of water vaporized during experiment, grams

W_i = initial weight of desorption apparatus plus water sample, grams

W_f = final weight of desorption apparatus and remaining water at end of run (t_f), grams

n = total number of samples withdrawn from apparatus

Δm = individual sample size withdrawn from apparatus, grams.

The water content at any time, t, is computed by:

$$M_t = M_o - \Delta M(t/t_f) \qquad (17)$$

where t_f = experiment run time, minutes.

Water in the "as procured" condition (i.e., with interfering chemical species if originally present) is vaporized at a constant rate if temperature, air humidity, air rate, liquid rate remain constant throughout the run. Table 3 contains an example of the raw data.

The raw experimental data appears in the Appendix.

Data analysis techniques with individual species tests or single pure components in water – The quantity of species i in the wastewater sample (X_{io}) is obtained from the initial sample withdrawn before the desorption experiment is performed. Equation (10) is the mathematical tool employed to obtain the relative volatilization rate (i.e., K_i/a) of species i. K_i/a can be obtained graphically by preparing a log-log plot of X_{it} and (M_o/M_t) as directed by Equation 10. The slope of a straight line through these raw data points yields $(K_i/a - 1)$. Approximately the same result can be achieved by the use of linear regression. Equation (10) is linear and of the form:

$$Y = a + bX \qquad (18)$$

where $Y \equiv \log X_{it}$,

$a \equiv \log X_{io}$,

$b \equiv -(K_i/a - 1)$,

$X \equiv \log [M_o/M_t]$.

TABLE 3

Typical Desorption Experiment Raw and Transformed Data-Fibers, Chemical and Plastic Industry Sample

A. Raw Data			B. Transformed Data			
t, time (min.)	M_t, water (grams)	C_t, organic (mg C./l)	M_t/M_o	C_t/C°	F_t	ϕ_t
0	300.	452	1.000	1.000	1.000	1.000
5	296.5	432	.9883	.9558	.9446	.8448
10	293.	413	.9767	.9137	.8924	.6986
20	286.	397	.9533	.8783	.8373	.5443
30	279.	379	.9300	.8385	.7798	.3832
40	272.	375	.9067	.8296	.7522	.3059
50	265.	361	.8833	.7987	.7055	.1751
55	261.5	365	.8717	.8075	.7039	.1706
60	258.	366	.8600	.8097	.6964	.1496
∞			.0		F°_{nv} = .643	

Multiple linear regression computer software packager can be employed to yield K_i/a plus statistical information related to the best fit straight line correlation (i.e., t-test on significance of the slope, standard error of the estimate, multiple correlation coefficient, etc.). Such a software package was employed in all computations of K_i/a in this work.

It should be pointed out that the above procedures can also be employed with gross pollutant measures (i.e., BOD_5, COD and TOC) on simulated wastewater consisting of *single* pure components in distilled water (i.e., methanol in water). The above procedures *should not be used* if the simulated waste consist of a mixture of pure components added to distilled water.

Data analysis techniques with gross pollutant measures of pure component mixtures and wastewater samples – A pseudo relative volatilization rate (i.e., K_s/a) and the original volatile fraction (F_v°) of a simulated or actual wastewater sample may be obtained from the data of a single packed column desorption experiment. Equations (14) and (15) are the directives by which this data can be obtained. A graphical data analysis technique or an analytical data analysis technique may be employed. Prior to employing either technique the raw concentration data (i.e., C_t) must be transformed to F_t by:

$$F_t = (C_t/C^\circ) \bullet (M_t/M_o) \tag{19}$$

The graphical technique employs the directive of equation (14) and a plot of F_t vs (M_t/M_o) is made on Cartesian coordinate graph paper. The resulting plot should be similar to the one shown in Figure 3. The non-volatile fraction (i.e., F_{nv}°) can be estimated by visually extrapolating the data curve to $M_t/M_o = 0$. The volatile and non-volatile fractions are related:

$$F_v^\circ + F_{nv}^\circ = 1 \tag{20}$$

Once the non-volatile fraction has been obtained equation (15) can be employed to obtain K_s/a. A log-log plot of ϕ_t vs. (M_o/M_t) yields a line from which K_s/a can be obtained. Reinhardt (19) points out that the K_s/a is not necessarily constant if the waste contains a mixture of components of widely varying relative volatilities. He further points out that a slope obtained at M_t/M_o near unity is indicative of the highly volatile components while a slope obtained at the low value of M_t/M_o is representative of the less volatile components. A non-linear plot, therefore is an indication of more than one volatile organic component in the wastewater sample.

An analytical technique was developed to obtain F_{nv}° and K_s/a. This analytical technique was improvised to alleviate the extrapolation step necessary in the graphical procedure. If K_s/a is small, the extrapolated estimate of F_{nv}° is very difficult to estimate

with any degree of certainty. The calculated results shown in Figure 3 reveal that in a normal sixty minute run (i.e., $M_t/M_o \sim .85$) F_t is far removed from $F^\circ_{nv} = .2$ for $K_s/a \leq 5$.

The analytical technique is based upon the heuristic notion that there is a unique value of K_s/a and equation (15) will be a "best fit" to the transformed experimental data (ϕ_t vs. M_o/M_t) in a least squares sense. A computer algorithm has been developed which performs a one dimensional search (Golden Section) for F°_{nv} on the range [0.0, F_t (min.)]. The algorithm produces the unique values of F°_{nv} and K_s/a when the coefficient of variation is a minimum. The coefficient of variation is given by:

$$CV = SE/(K_s/a) \tag{21}$$

where CV = coefficient of variation

SE = standard error of estimate of correlating equation (15)

K_s/a = least squares slope of correlating equation (15)

This "non-volatile fraction" computer algorithm is reproduced in the appendix along with documentation for its use.

Wastewater Samples Employed

Simulated wastewater samples – A total of fifteen (15) pure chemicals were employed on this project. These pure components were combined with water singly or in mixtures to create wastewater of various volatilities and volatile fractions. The starting concentrations were adjusted roughly to 1000 ppm total carbon content. The pure components employed were:

acetaldehyde	phenol
acetone	formic acid
iso-propanol	ethanol
methanol	ammonia
normal-propanol	benzene
furfural	styrene
propionic acid	sucrose
acetic acid	

Industrial wastewater samples – A total of nineteen (19) industrial wastewater samples representing fifteen different industry types were tested in the laboratory desorption apparatus. These samples were obtained directly from industry personnel, from local city

wastewater treatment plant operators and a local engineering consultant. The industry types and major product represented by samples are:

poultry, liquid egg
poultry, turkey processing
poultry, broiler processing
metal, hand tool manufacture
petroleum production, oilfield blowpit
canning, grape products
pharmaceutical, specific product unknown
paper, unbleached kraft
paper, tissue and plywood
food, margarine–shortening
petroleum, refined petroleum products
petrochemical, 1, 3 butadiene
petrochemical, 1, 2 dichloroethane
paper (bleached), pulp and kraft paper
fibers, chemicals and plastics

Combined wastewater samples – A total of two samples were obtained of combined industrial and municipal wastewater. These samples were obtained prior to the primary treatment unit from:

City of Fayetteville, Arkansas Pollution Control Plant
City of Springdale, Arkansas Wastewater Treatment Plant

SECTION VII

EXPERIMENTAL PHASE AND RESULTS

Physical Experimental Results with Pure Components and Simulated Wastewater

Desorption in packed columns is a well established process in both the theoretically and practical aspects. Since this knowledge is readily available only selected experiments need be performed to confirm the predicted behavior of this proposed desorption device. Equations (3), (7) and (10) constitute the critical packed column, batch desorption relationships. The predictions of these equations must be verified by physical experiment in order that desorption data be interpreted in the proposed fashion. Equation (3) predicts that K_i is independent of the concentration of component i and dependent only upon the column, flow rates and species relative volatility. Equation (7) predicts that water is evaporated from the column at a constant rate dependent upon the same type parameters. Equation (10) predicts a log-linear relationship between the concentration of component i and water in a batch desorption experiment if K_i and a are indeed constant.

An extension of the above theory to aqueous systems containing more than one dissolved component has been constructed based on the validity of the single component model. In general, wastewater can be envisioned to contain volatile components (i.e., $K_i > 0$) of a quantity fraction, F°_v, and non-volatile components (i.e., $K_i = 0$) of a quantity fraction, F°_{nv}. Equation (14) predicts the general desorption behavior of a wastewater containing volatile and non-volatile organic components.

Selected pure components were chosen to verify the proposed desorption analytical model. Pure components were chosen based on relative volatilities and on the occurrence of the species in industrial wastewater. A total of fifteen pure components were employed in various desorption experiments. Selected pure components were combined to fabricate a "simulated wastewater" with a volatile and non-volatile character.

Raschig Ring Packed Desorption Column – A total of approximately twenty five experiments were performed with single pure components and simulated wastewater with the raschig ring column. Four test techniques were employed to obtain concentration of the remaining organics in the samples. Selected experimental results are shown in Figures 6 through 9. A straight line relationship was the dominant behavior in *all* experiments with single pure components when plotted as directed by equation (10). Table No. 4 contains the relative volatilization rate data for the pure component experiments. All experimental data was processed on a linear regression computer program and statistical data was generated. Table 5 contains selected statistical parameters of the various experiments.

Three simulated wastewater experiments were performed with the raschig ring column.

TABLE 4

Relative Desorption Rates of Selected Pure Components With Raschig Ring Column

Constituent	Experimental K*/a				
	TOC	BOD(5)	COD	GC	Theoretical K/a
acetaldehyde	207.	207.	171.	–	186.
acetone (run 1)	51.8	98.8	85.8	55.8	46.3
acetone (run 2)	99.7	36.1	45.6	48.4	42.1
i-propanol	15.2	2.73	10.7	–	42.3
methanol (run 1)	21.2	7.29	8.91	7.73	28.4
methanol (run 2)	10.98	13.11	8.84	10.21	20.7
n-propanol	12.4	22.6	14.8	–	16.0
n-butanol	10.4	11.0	18.3	–	6.18
furfural	–	–	10.0	–	–
propionic acid	.37	1.51	0.00	–	4.00
acetic acid	2.23	4.81	1.00	–	2.29
phenol (run 1)	.733	1.91	.557	–	1.00
phenol (run 2)	1.49	1.13	.977	–	1.13
formic acid	6.99	–	–	–	1.12

*K is the specific desorption rate of the organic component

a is the specific desorption rate of water, both in a 45 cm ht x 5 cm diameter, Raschig ring, packed air stripping (desorption) column.

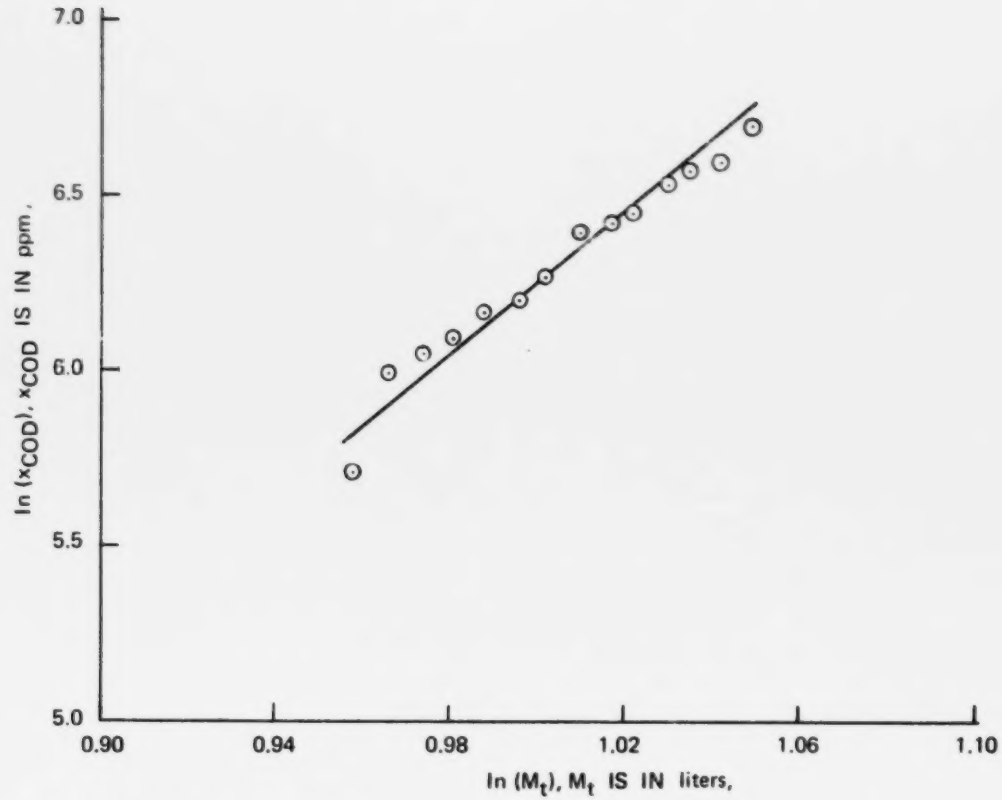


Figure 6. Desorption of methanol in water with Raschig Ring Column – COD analysis

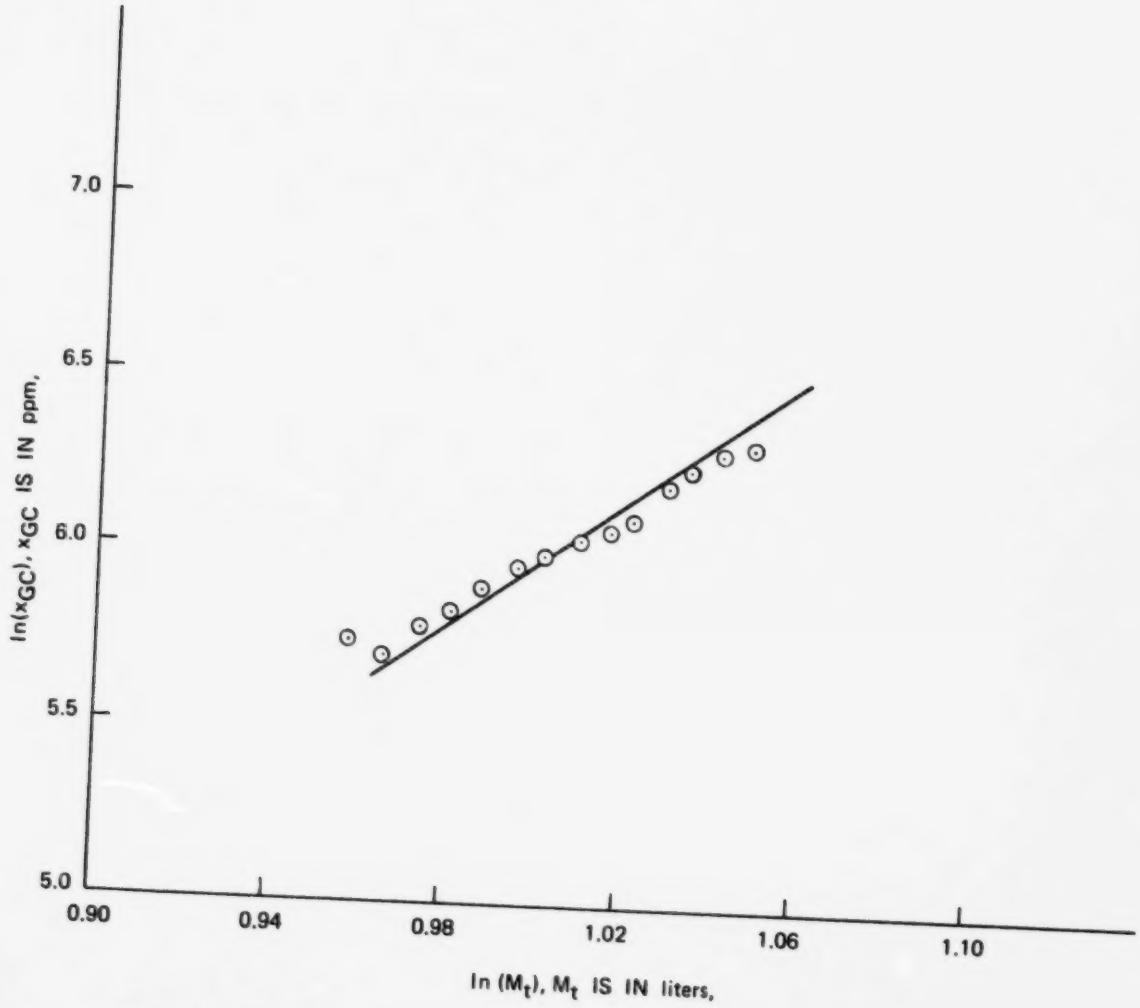


Figure 7. Desorption of methanol in water with Raschig Ring Column – GC analysis

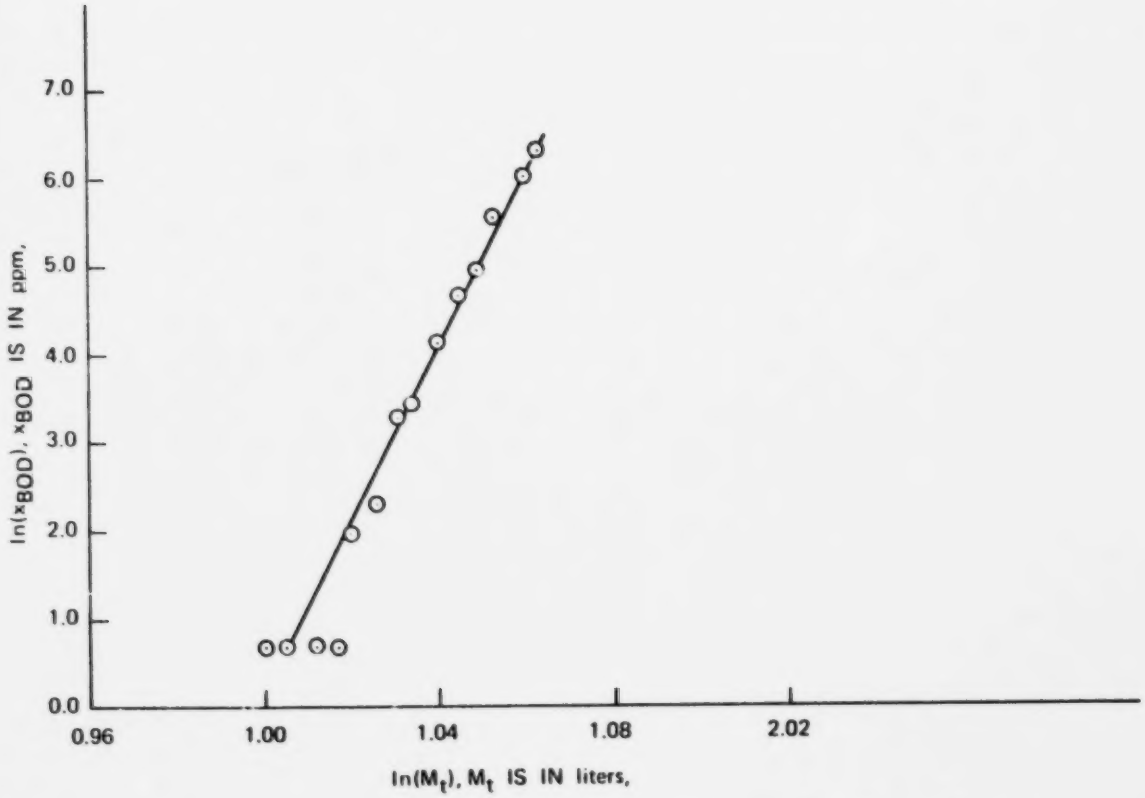


Figure 8. Desorption of acetone in water with Raschig Ring Column – BOD_5 analysis

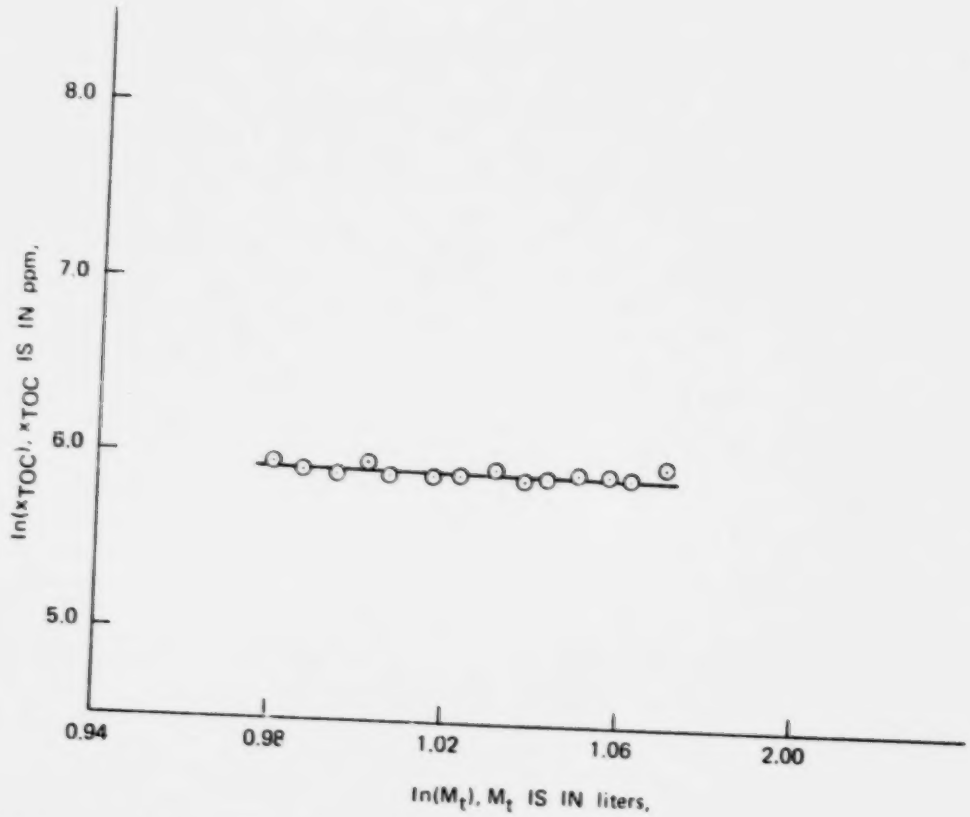


Figure 9. Desorption of phenol in water with Raschig Ring Column – TOC analysis

TABLE 5

Raschig Ring Experiments Linear Regression Statistical Data for Pure Components

Analysis	Standard Error Estimate		Multiple Correlation Coefficient		t value for K/a – 1	
	(Exp. 1)	(Exp. 2)	(Exp. 1)	(Exp. 2)	(Exp. 1)	(Exp. 2)
Methanol-Water						
COD	0.054,	0.555	0.976,	0.974	15.5117,	15.0396
GC	0.049,	0.081	0.973,	0.960	14.6462,	11.8275
TOC	0.257,	0.070	0.923,	0.974	8.3318,	14.8747
BOD	0.101,	0.114	0.885,	0.955	6.5929,	11.1035
Acetone-Water						
COD	1.021,	0.554	0.811,	0.940	3.6723,	8.7106
GC	0.704,	0.439	0.777,	0.892	3.0264,	4.4075
TOC	0.698,	0.704	0.680,	0.916	1.6050,	4.5585
BOD	0.885,	0.474	0.909,	0.919	6.9085,	8.0884
Phenol-Water						
COD	0.020,	0.016	0.563,	0.043	-2.3625,	-0.1492
TOC	0.028,	0.053	0.279,	0.269	-1.0079,	0.9662
BOD	0.030,	0.045	0.679,	0.089	3.2048,	0.3095
Acetic Acid						
TOC	.0463		.543		2.15	
BOD	.0463		.894		6.64	
COD	.0492		>.029		- .0962	
Formic Acid						
TOC	.152		.384		.721	
Propionic Acid						
TOC	.0749		.293		- .810	
BOD	.129		.142		.379	
COD	.0467		.617		-2.07	
Acetaldehyde						
TOC	.354		.949		8.52	
BOD	.665		.807		3.62	
COD	.375		.920		6.64	
n-propanol						
TOC	.048		.987		22.9	
BOD	.201		.940		10.3	
COD	.044		.992		30.1	
i-propanol						
TOC	.135		.913		8.39	
BOD	.391		.094		.354	
COD	.110		.882		6.99	

Simulated wastewater No. 1 consisted of ~500 ppm acetone and 500 ppm phenol added to distilled water. Simulated wastewater No. 2 and No. 3 consisted of approximately 330 ppm acetone, 330 ppm phenol and 330 ppm methanol in distilled water. Figures 10, 11 and 12 show the test results for these two simulated wastewaters.

The above experiments with single pure components and simulated wastewater demonstrated that the general behavior of the experiment results are as predicted by the desorption model equations. The log-log straight line behavior of single pure components was as predicted. The volatile and non-volatile multiple component behavior was qualitatively correct also. The quantitative data shows much variation and this is attributed mainly to the water evaporation lost from the apparatus. Average water loss for a 180 minute run was 253 grams with a range of 217 to 348 grams for a percent deviation range of −14.2% to + 37.5%. The errors inherent in accurately quantifying the water evaporated initiated a search for a more satisfactory desorption device. Other operational problems included; flooding due to pressure surges in air line, uncertainty in inlet air relative humidity, inability to control column temperature, three hour run time, and equipment bulkiness.

Intalox Saddle Packed Desorption Column – Three models of a laboratory scale desorption column were attempted before the design shown in Figure 5 was adopted. Glass shot .318 cm. O.D. (1/8 inch) was tried as a packing but proved to be inadequate at the high gas/liquid ratios desirable of a short experiment time. Run times of one hour were used on virtually all experiments performed with this column. The adoption of this device simplified the experimental procedure and improved the accuracy of the desorption results. The average water loss in a 60 minute run was $\Delta M = 40.4$ grams with a range of 38.5 to 42.2 grams. The percentage deviation range was −4.7% to + 4.5%. The initial charge volume was 300 grams of water.

Additional pure component experiments were performed with the Intalox saddle desorption column. Figure 13 contains data on four successive runs with normal butanol. These data give some indication of the reproducibility of the experiment. A graphical eye-estimated slope of $K_i/a - 1 = 8.11$ (see equation 10) is representative of all four runs. The relative volatilization rate for normal butanol (i.e., K_i/a) is 9.11. Similar plots for ammonia, benzene, styrene and sucrose yielded K/a values of 7.44, 79.2, 96.3 and 0.687 respectively.

Faulty data analysis and calculation techniques can have a significant effect on quantifying the volatile fractions in wastewater. Figure 14 shows the effect of stripping a 1000 ppm sucrose solution for three hours in the Intalox Saddle desorption apparatus. Since sucrose is non-volatile it should remain in the apparatus. A concentration (i.e., C/C_o) plot shows the carbon content to increase with time while a quantity plot (i.e., F_t) shows the carbon content remains constant. A +65% error is evident in the case of sucrose for a three

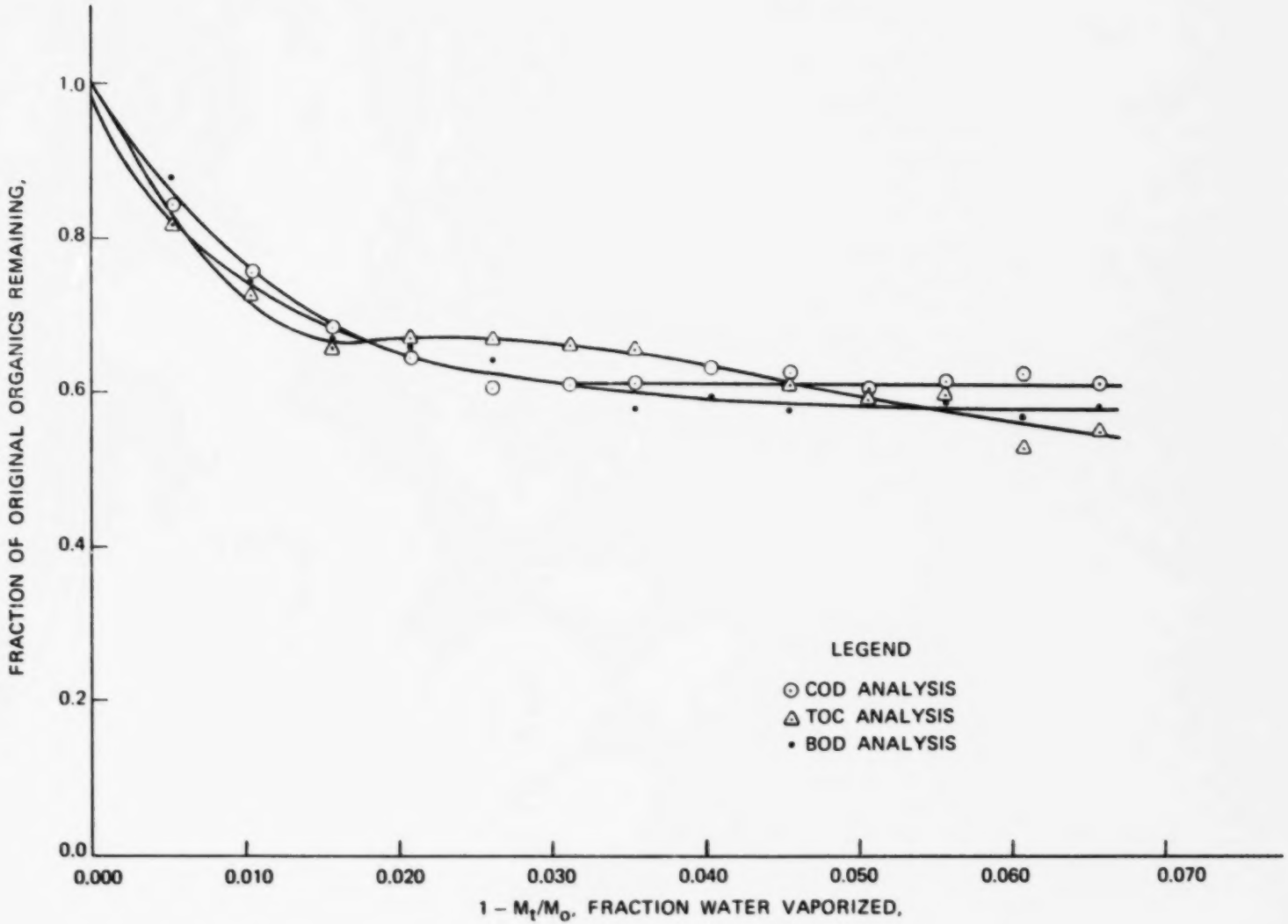


Figure 10. Desorption of simulated wastewater No. 1 with Raschig Ring Column.

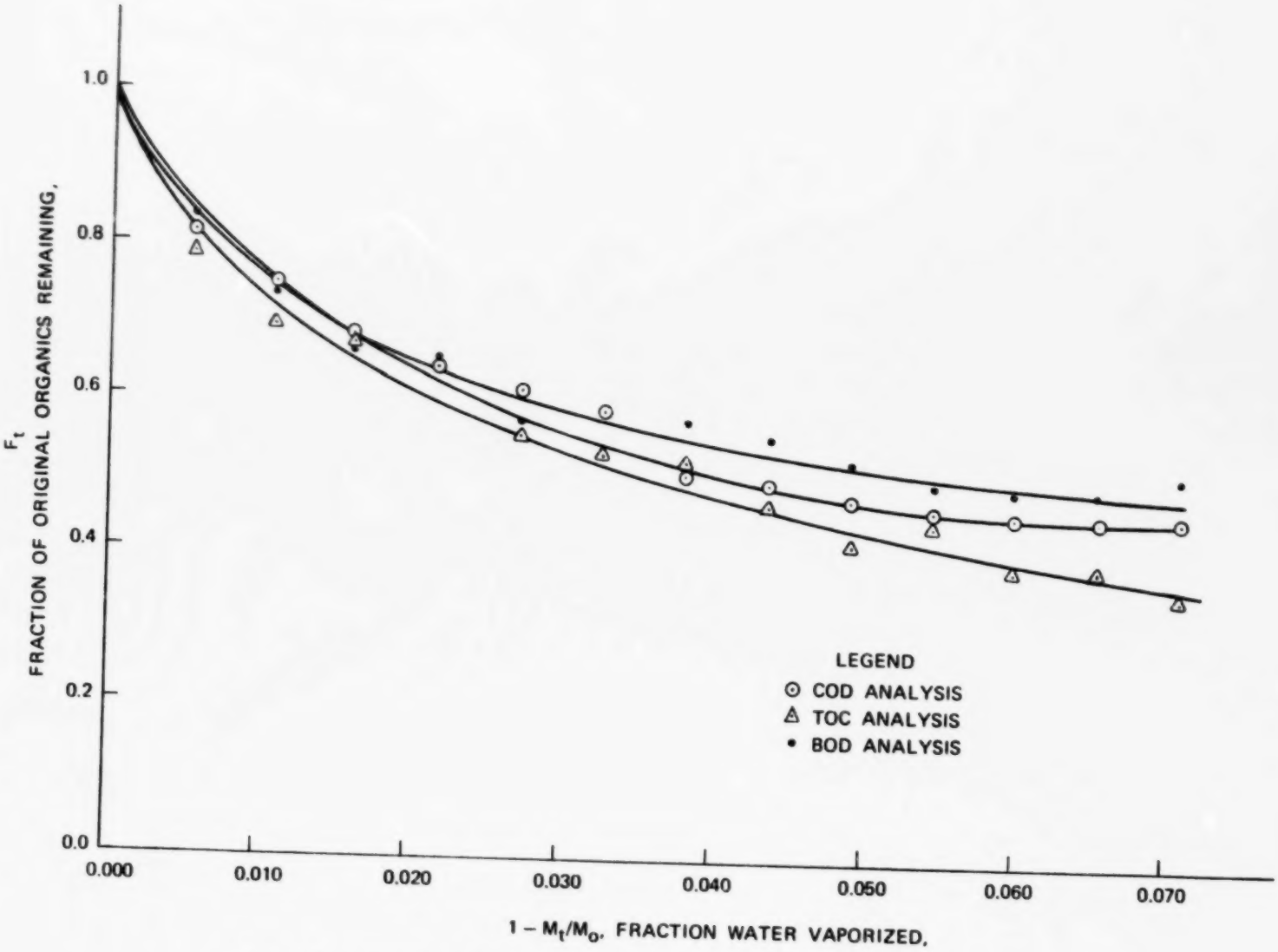


Figure 11. Desorption of simulated wastewater No. 2 in Raschig Ring Column,

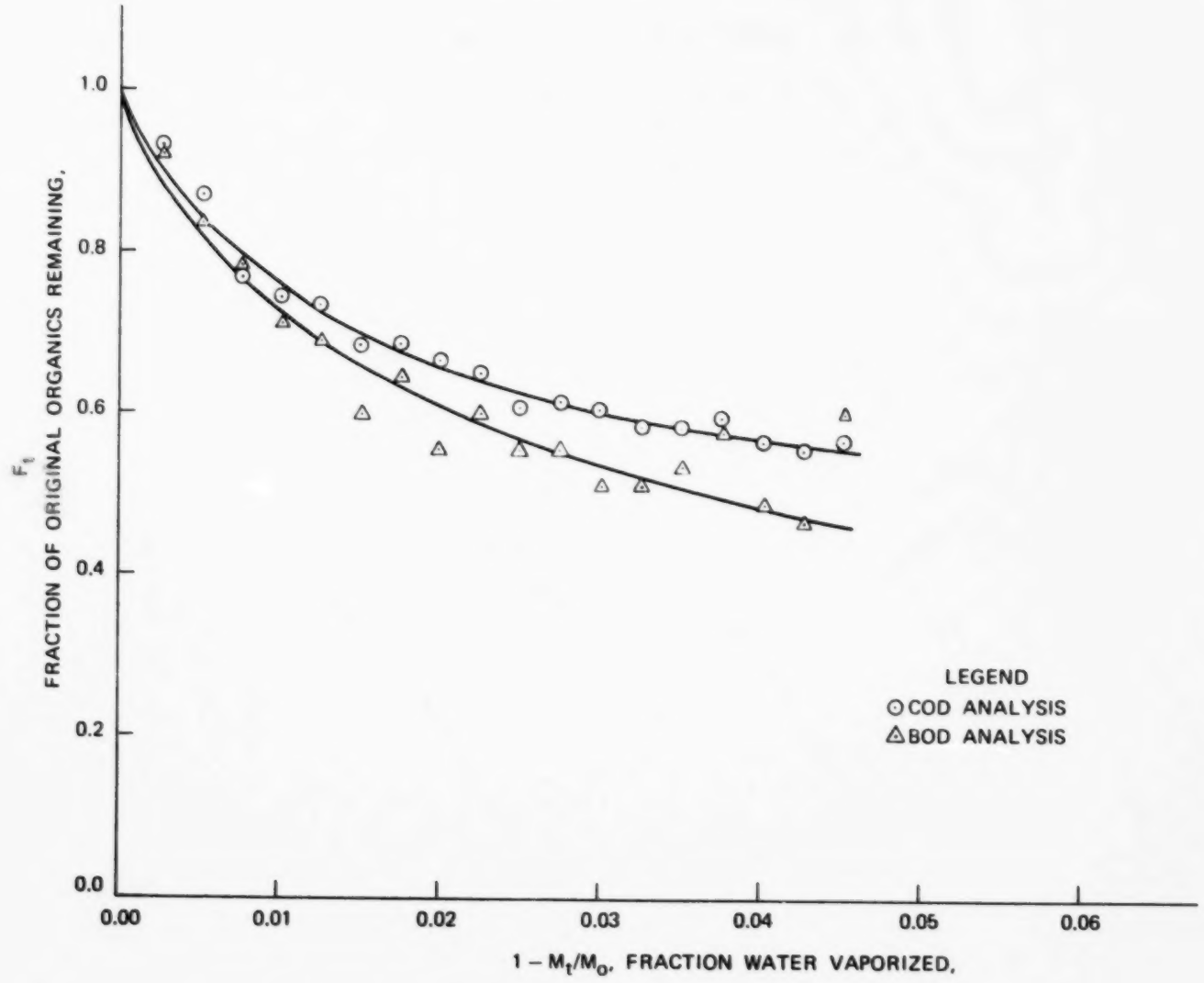


Figure 12. Desorption of simulated wastewater No. 3 with Raschig Ring Column.

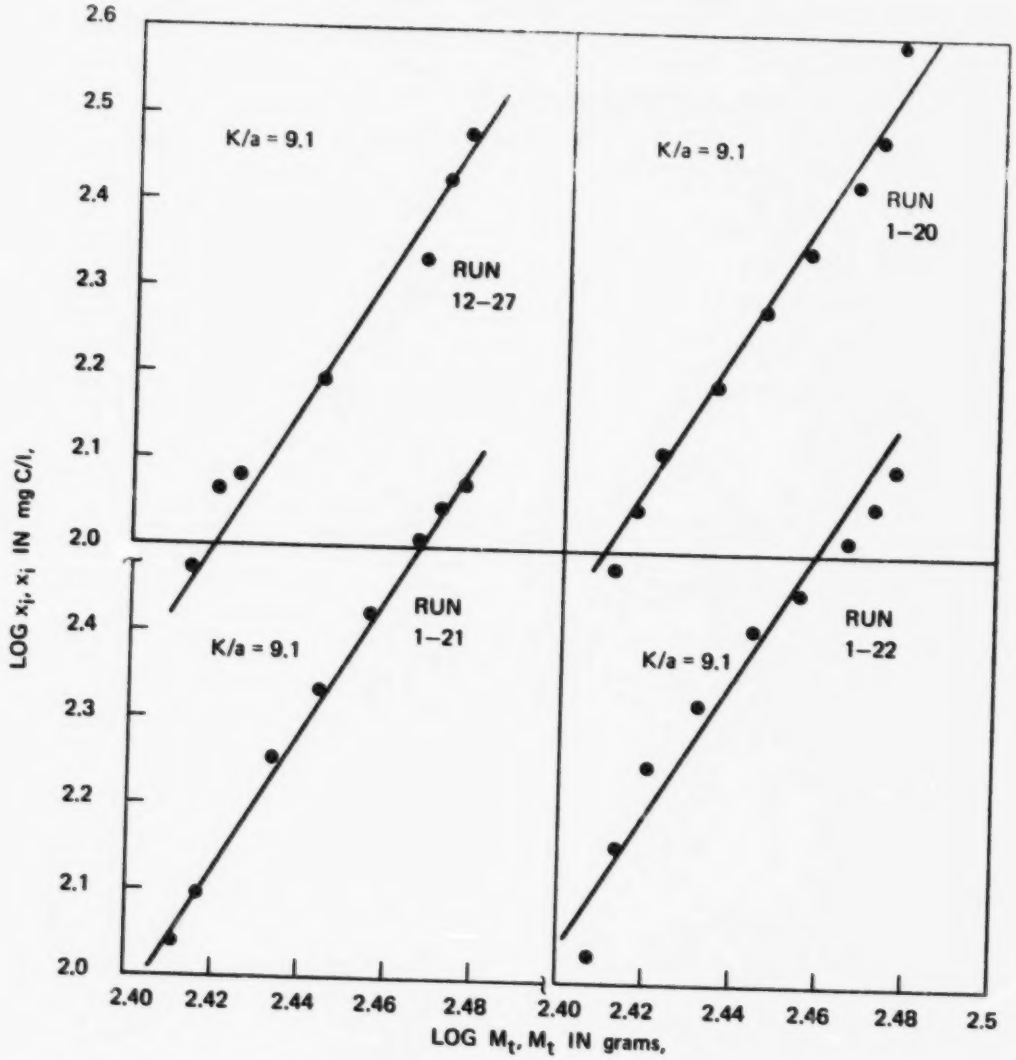


Figure 13. Desorption of n-Butanol in Intalox Saddle Column — TOC analysis

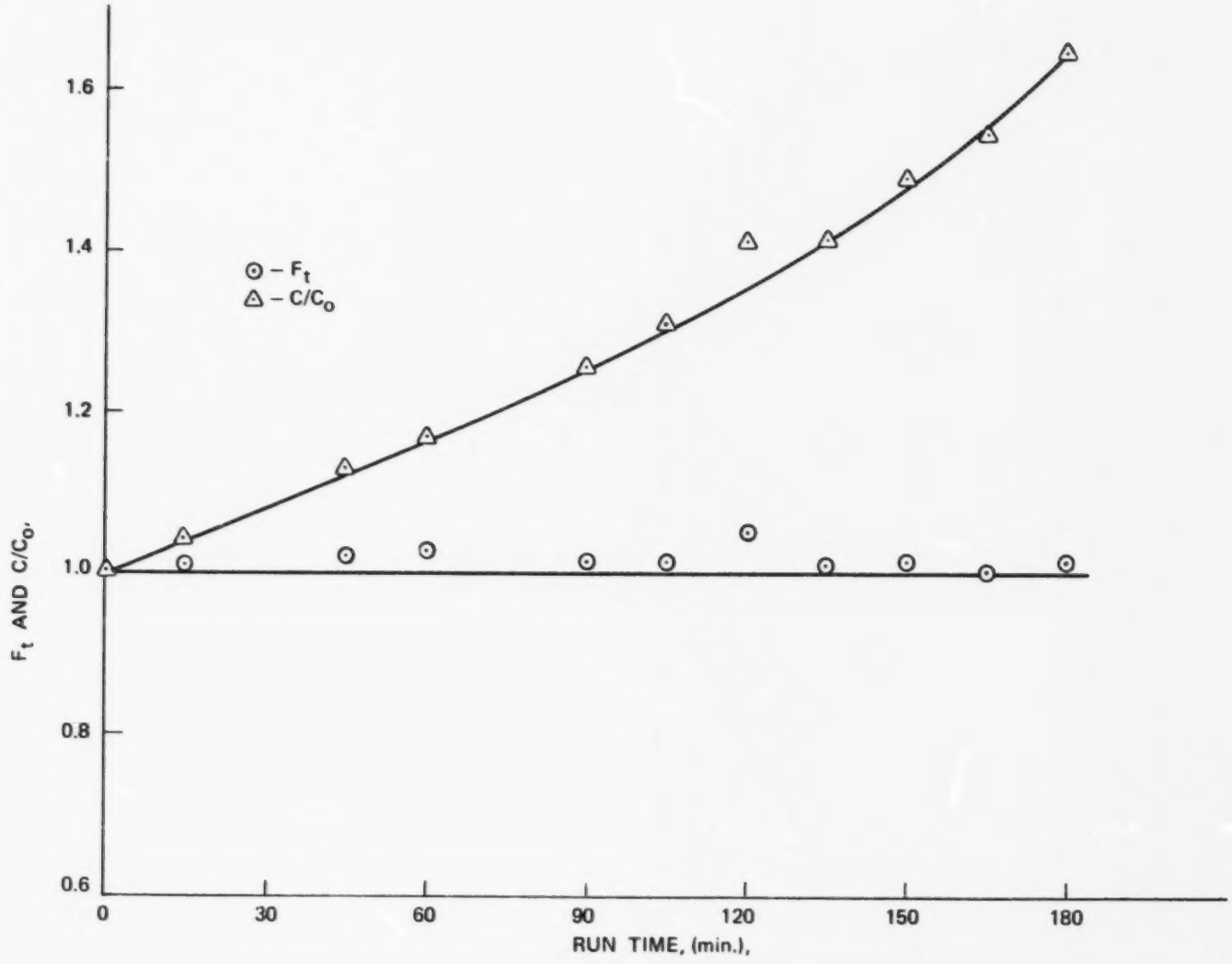


Figure 14. Desorption of sucrose solution in Intalox Saddle Column – TOC analysis

hour run. Figure 15 shows the magnitude of discrepancy encountered when concentration is employed rather than quantity on a normal one hour experiment with a poultry processing industry wastewater. As run time increases the error increases.

A series of three experiments were undertaken to determine if certain compounds could affect the desorption test results. Since desorption is an interphase mass transfer process, compounds were selected which have been known to interfere with the transfer process. Certain substances tend to concentrate at the interface, and may hinder the interphase transfer of solute. Cetyl alcohol, when spread upon water in remarkably small concentrations reduces the rate of evaporation of water into air by as much as 95% (18). Surfactants, such as sodium tetradecyl sulfate (NaTDS) suppresses convection by inhibiting flow at the interface (21). Goswami (11) reports that Na_2HPO_4 reduces the aldehyde desorption rate. However, this is in conflict with a referenced report that it increased COD removal in a refinery wastewater from 72 to 90%. Normal butanol was desorbed in the Intalox Saddle device in the presences of: 30 ppm (volume) cetyl alcohol, 50 ppm (volume) NaTDS and 30 ppm (volume) Na_2HPO_4. Figure 16 contains the experimental data for these interference compounds. Cetyl alcohol appears to effect the desorption slightly. The desorption effect of the other two compounds is not significant.

A gas-chromatograph (GC) may be employed to determine the concentration of some organics in wastewater. A simulated wastewater was fabricated consisting of known volatile and non-volatile species. Simulated wastewater No. 4 consisted of equal parts (~ 165 ppm) sucrose, phenol, n-butanol, acetic acid, acetaldehyde and acetone. Desorption was performed in the Intalox Saddle device and GC was used to detect the total organic concentration. The sum total area of all components was employed; no attempt was made to obtain the concentration of individual species. The remaining organic fraction is:

$$F_{t,A} = (A_t/A_o) \bullet (M_t/M_o) \qquad (22)$$

where $F_{t,A}$ = gas chromatograph organic fraction remaining

A_t = total integrator output area at time t, cm^2.

A_o = total integrator output area at time initial, cm^2.

Figure 17 shows the test results obtained with the 15% Chrom-W column. Sucrose, phenol and acetic acid are non-volatile yet >90% of the GC-apparent organics are desorbed in a one hour run. Gas chromatographic analysis techniques employing total integrated area output as a measure of organic concentration will yield high values of the volatile fraction since the non-volatile high molecular weight components may go undetected.

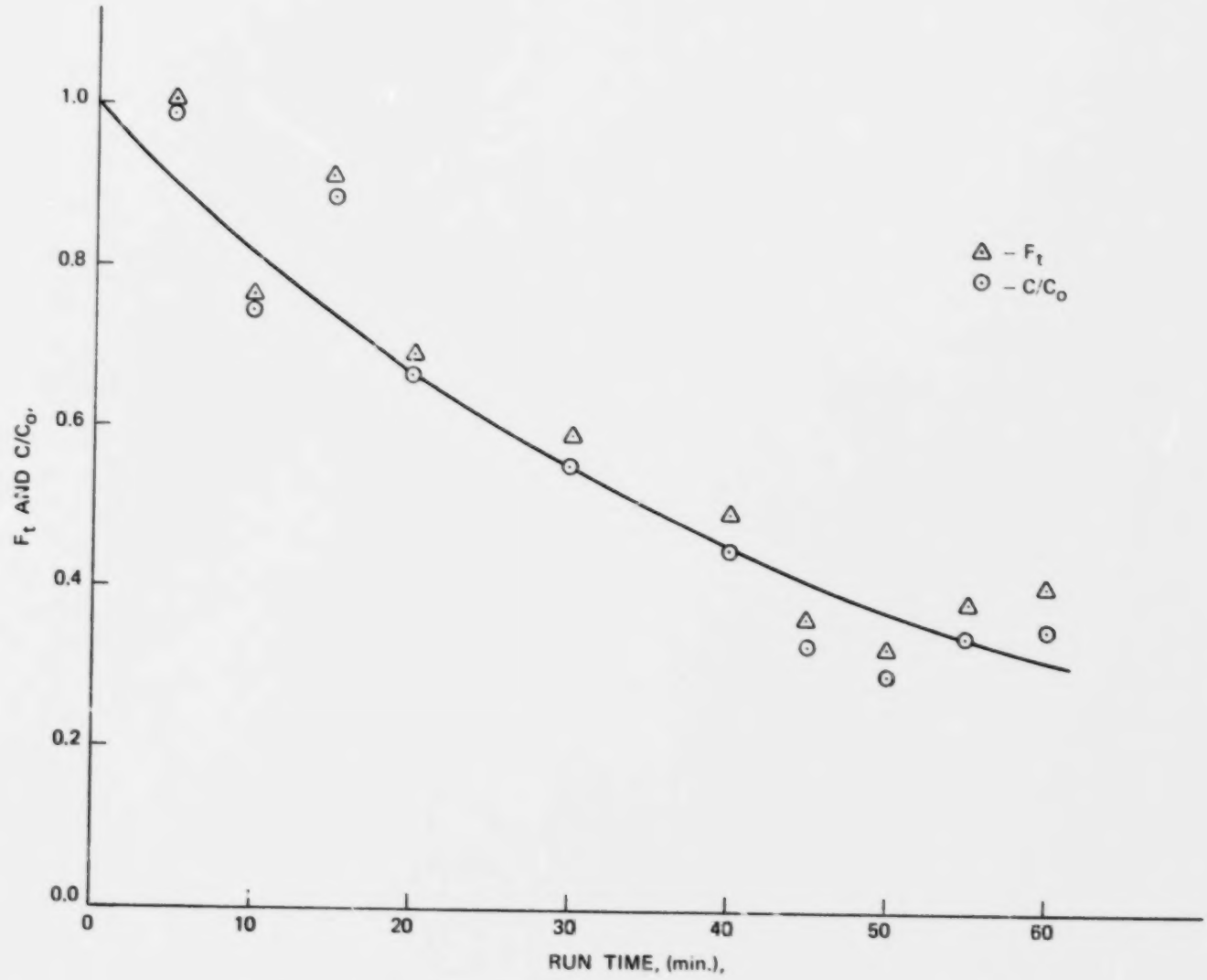


Figure 15. Desorption of poultry processing wastewater in Intalox Saddle Column – TOC analysis

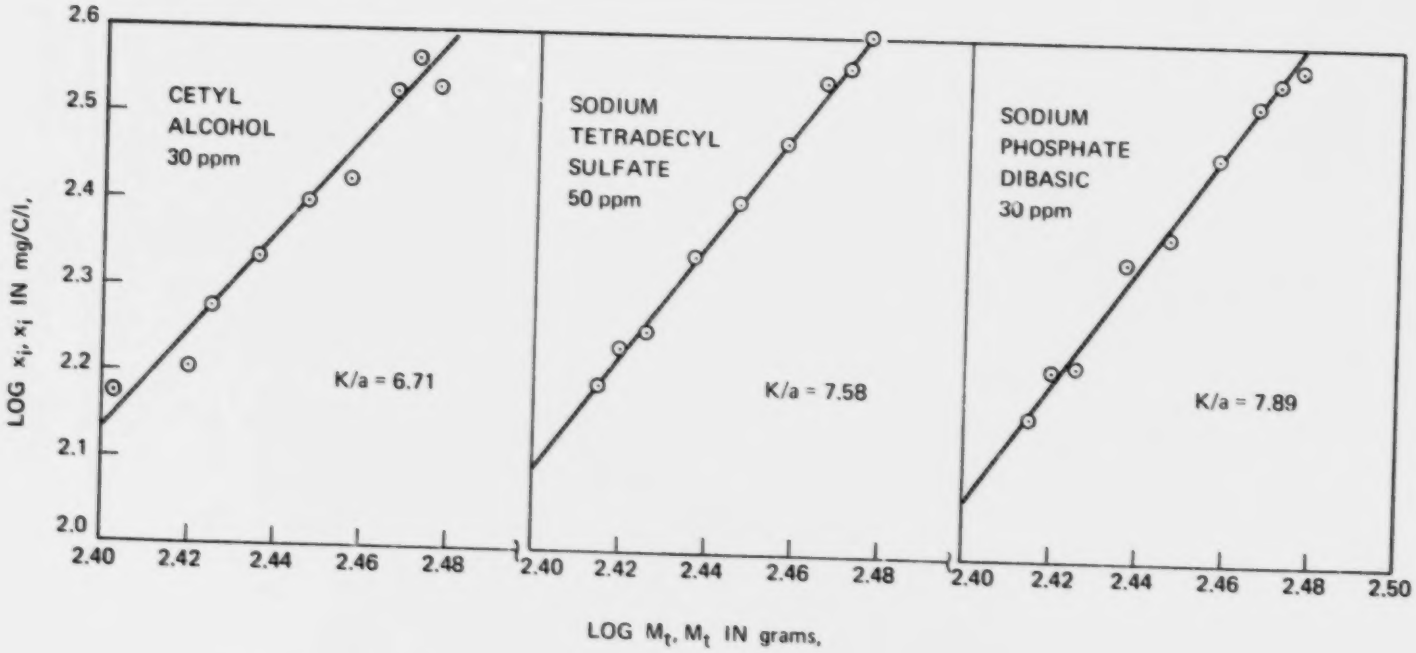


Figure 16. Desorption of n-Butanol in Intalox Saddle Column — TOC analysis

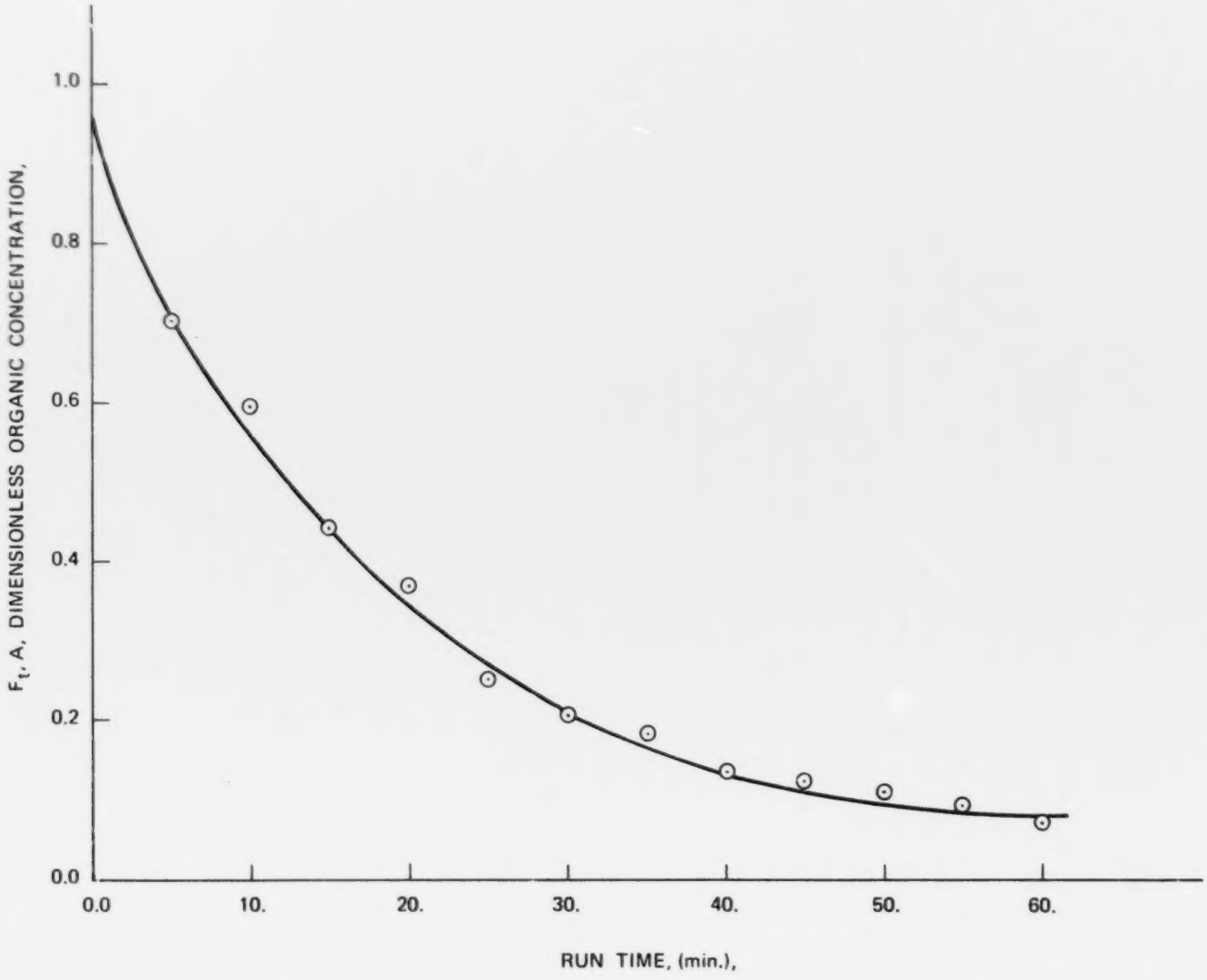


Figure 17. Desorption of simulated wastewater No. 4 with Intalox Saddle Column – GC analysis.

Analytical Experiment Results

It was mentioned at the beginning of this section that the science of desorption in packed columns is well established. The foregoing experimental results verify the important predictions of the desorption model equations. In this section the mathematical equations of packed column desorption will be employed to study aspects of the experimental apparatus which would require prolonged laboratory experimentation to verify. Equations (3) and (7) constitute the important desorption model relationships and will constitute the "experimental apparatus" in this section of the report.

Raschig Ring Analytical Model Results – Model equations (3) and (7) were employed with the apparatus dimensions and operating conditions of the Raschig Ring desorption apparatus. This device did not have means of temperature control. Therefore, the calculations of K/a were performed at actual operating temperature and not at 25°C. The inlet relative humidity for the calculations is assumed to be 0%, however there is some doubt whether this condition was consistently maintained during all the experimental runs. Table 4 contains the calculated K/a values and are listed under the column titled: "Theoretical K/a". In general the analytical model does a fair job in predicting the relative volatilization rate of pure components.

Temperature and relative humidity is considered to have a large effect on the relative volatilization rate. Equation (7) was employed to study the effect of column temperature and inlet air relative humidity on the fraction of water lost in the column. Figure 18 shows the effect of temperature and % relative humidity is significant. These predicted results stimulated a search for a means of maintaining a high degree of control over the temperature and relative humidity during the experiment.

Intalox Saddle Analytical Model Results – Model equations (3) and (7) were employed with the apparatus dimensions and operating conditions of the Intalox Saddle desorption device. Column temperature is maintained at 25°C ±1°C by means of heating tape or a rheostat controlled hotplate and dry bottled air is employed with the Intalox Saddle device. We became concerned with the wide variation in liquid flow rate and the effect it may have on the relative volatilization rate. We attempted to maintain a liquid flow rate at or near 150 ml./min. Uncontrollable changes in the pumping head, etc., caused the actual measured rate to fluctuate between 130 and 160 ml./min. Employing the analytical model of the experimental desorption apparatus, the effect of L(l/min) on K/a for n-butanol was studied. Figure 19 shows that there is only a slight variation in K/a (2.4%) for a sizable variation in L(33.3%). Figure 20 shows a similar study of the effect of the dry air rate. A 10% variation in K/a was computed for n-butanol for an air flow variation of 75%. It appears that moderate deviations in liquid and air flow rates will have a relatively insignificant effect on

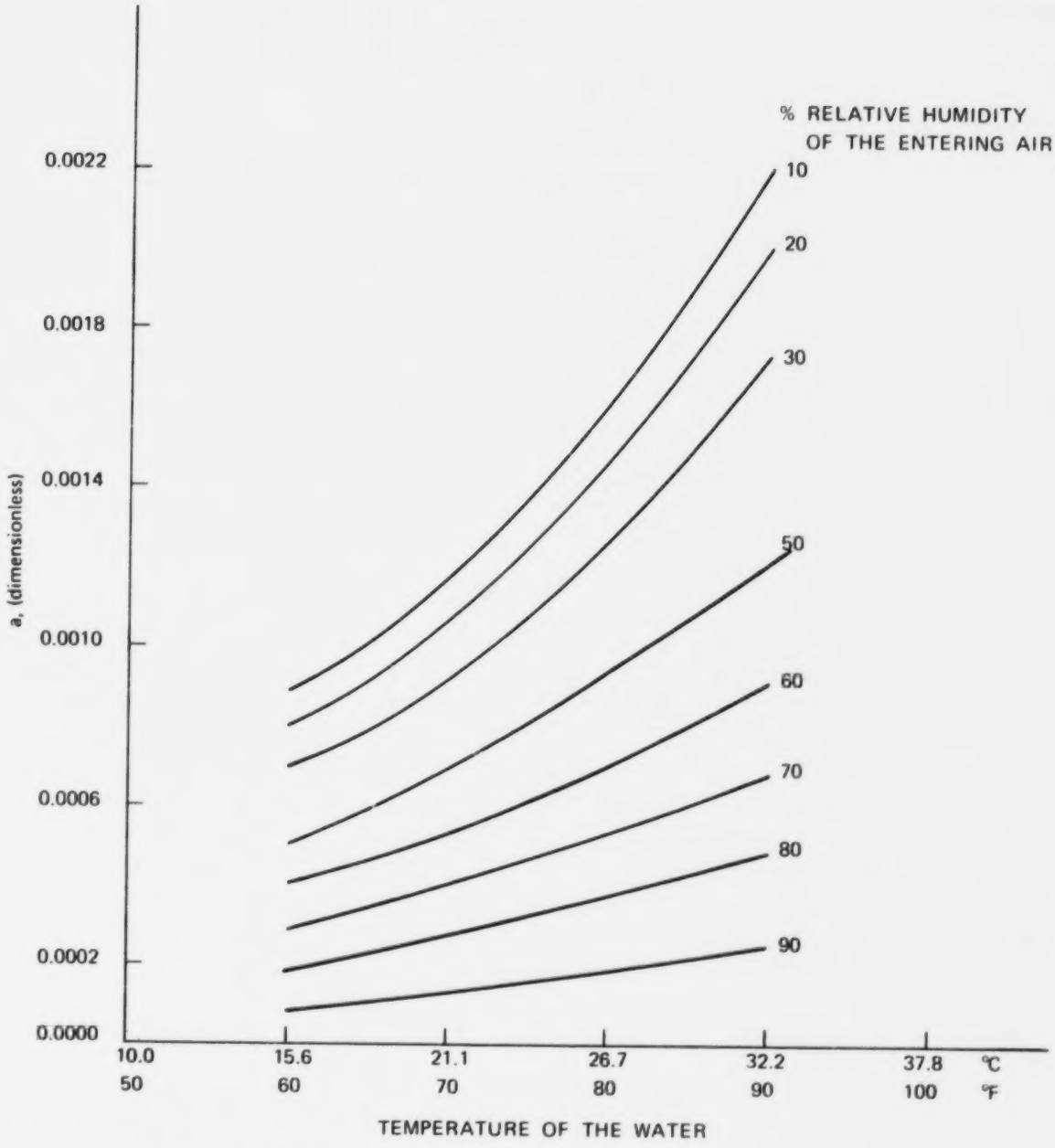


Figure 18. Water evaporation calculations in the Raschig Ring Column.

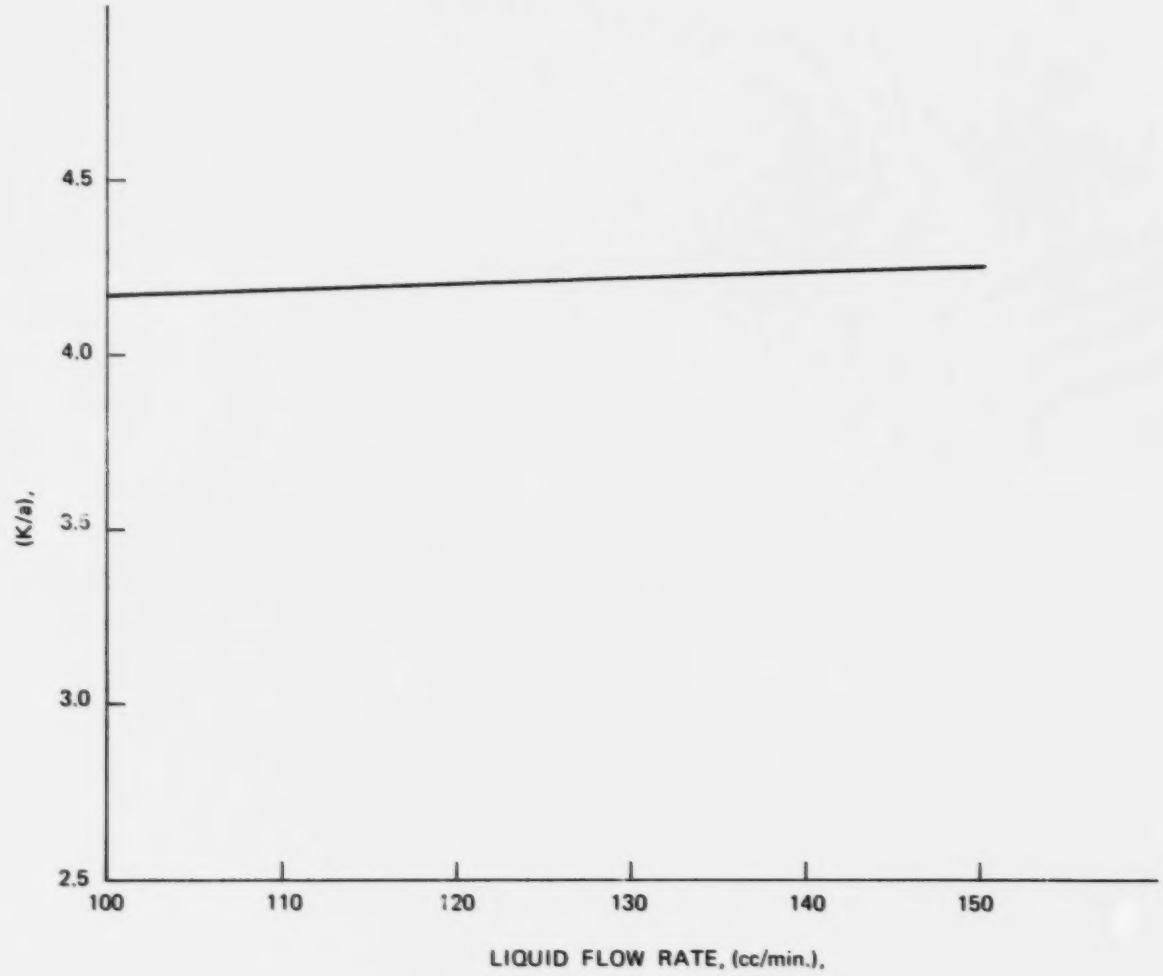


Figure 19. n-Butanol desorption calculations – effect of liquid rate.

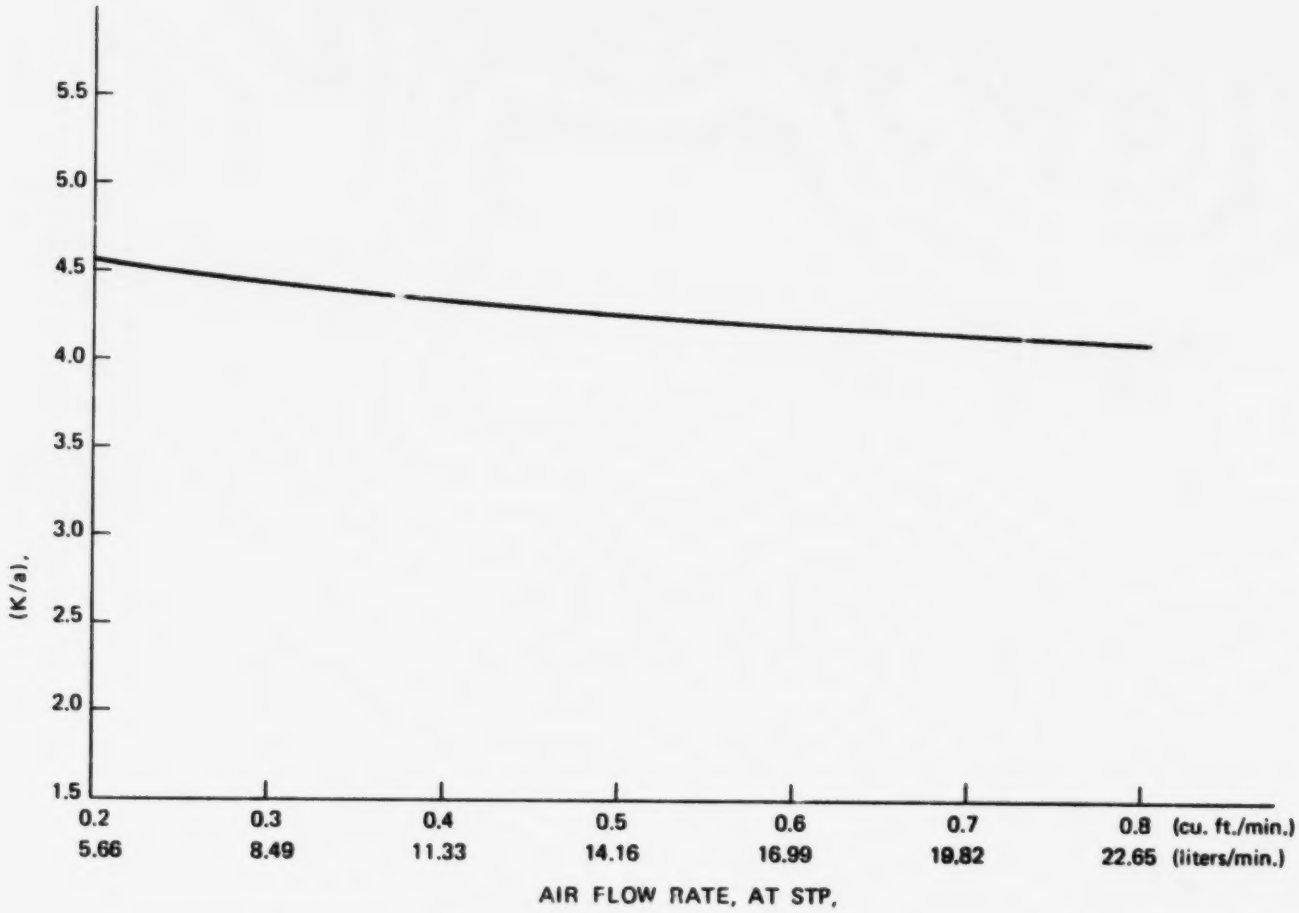


Figure 20. n-Butanol desorption calculations -- effect of air rate.

K/a, however increased rates tend to decrease the experiment run time.

Calculated results of the relative volatilization rate of pure components for the Intalox Saddle device are shown in Table 3. These calculated results indicate that the K/a equals the relative volatility for those components that are non-volatile in nature.

Calculations were performed to develop a correction factor relationship for an experimental relative humidity other than 0%. The analytical model results indicated that the air emerging from the Intalox Saddle packed column (15 cm. in height) was saturated with water and makes possible the following equation:

$$(K/a)_e \text{ @ } 0\%RH = (K/a)_e \text{ @ } E\%RH \times ((100 - E\%RH)/100) \qquad (23)$$

where $(K/a)_e$ @ 0%RH = the relative volatilization rate at 0%RH,

$(K/a)_e$ @ E%RH = the relative volatilization rate at the experiment relative humidity,

E%RH = the experiment percent relative humidity.

The experimental K/a result obtained when humid air is employed will be larger than the standard condition (i.e., 0% RH) value and the above equation should be employed as a correction to this standard.

Experiments With Industrial Wastewater Samples

Industry representatives responding favorably to our request (by letter) for wastewater samples were instructed to procure and handle the sample as follows:

quantity of sample: 500 ml.

container: small mouth plastic bottle

sample point: total wastewater effluent prior to any treatment operation (i.e., raw)

sample type: single grab aliquot during daytime under normal operating conditions

sample handling: adjust pH to 3.0 or lower, seal cap to bottle with electrical tape or other type of rubber tape that will stretch and form a vapor seal

sample information: fill in requested information and attach tag to bottle neck. Tag contains return address and stamps on face and general sample information on backside. (requested information was: industry type, major product and daily wastewater flow)

packaging: no special packaging is necessary. Attach tag to bottle neck.

mailing: place sealed, tagged bottle in U.S. Mail (parcel post).

A total of twenty seven letters were sent to industry representatives. Eight positive responses and three negative responses were obtained. No response was received from the

sixteen remaining inquiries. Samples received were both grab and composite types. All samples received arrived intact and seemed "fresh". No septic odor was detected.

Eight industrial samples composited (24 hr) by personnel from the City of Springdale, Arkansas, were obtained. Three industrial samples were obtained from McClelland Consulting Engineers, Inc., of Fayetteville, Arkansas.

All industrial samples were processed on the Intalox Saddle device. Three hundred gram samples were employed. Experiment run time was one hour. One milliliter samples were withdrawn every five minutes. TOC analysis was performed on all wastewater. A limited number of GC analysis were performed also. Fifty microliter (50 μl) samples were employed with the TOC and ten microliter samples were employed with the G C. Odor eminating from the desorption apparatus funnel was noted at various times during the run. Other details of operation are as reported in the METHODS section. All test results are reported at standard conditions (i.e., 25°C, ambient pressure, 0% R H).

Table 6 contains the experimental results of the nineteen industrial samples. Table 7 contains collaborative published data from which reliable volatile information could be obtained. Figures 21, 22 and 23 display the results of the desorption experiments for twelve of the industrial wastewater samples. Also shown in these figures is the computer program estimated ultimate non-volatile fraction (i.e., F°_{nv}). This extrapolated F_t value is plotted at $M_t/M_o = 0$.

Now, once F°_{nv} is obtained, it is possible to compute the relative volatilization rate for the pseudo single component fraction (see equation 15). Figure 24 shows representative results for four wastewater experiments. Drawn straight lines are computer generated. Wastewater data exhibiting a non-linear function are interpreted to typify a mixture of volatile components. Wastewater data exhibiting a linear function are interpreted to typify single volatile components or several components with identical relative volatilities.

Gas chromatographic analysis were performed on three industrial wastewater samples. Figure 25 shows the experimental data for a petroleum refinery wastewater. The GC data tends to show a larger fraction of volatiles than the TOC data. This type of behavior also occurred with simulated wastewater No. 4 (see Figure 17). The GC analysis tends to "see" only the low molecular weight constituents.

A significant odor reduction was noted as the run progressed on those samples which had a detectable initial odor. No foaming occurred during any experimental run with pure components or actual wastewater samples.

TABLE 6

Air-Volatile Fractions in Industrial Wastewaters

Industry Type, Major Product	Wastewater Flow 1000 ga/da	Raw Conc. mg/l	Volatile Fraction %	Relative Vol. Rate K/a	Source
poultry, liquid egg products	42.8	1545.	15.6	5.0	J–T[1]
poultry, turkey processing	960.	2.1	0.	–	J–T
poultry, chicken processing	360.	78.	4.1	–	J–T
poultry, chicken processing	622.	122.	98.0	10.6	J–T
poultry, chicken processing	547.	206.	0.	–	J–T
poultry, chicken processing	360.	80.	6.6	–	J–T
metal, hand tool mfg.	76.2	51.	0.	–	J–T
oil field blowpit	?	102.	19.4	9.3	J–T
canning, grape products	335.	202.	0.	–	J–T
pharmaceutical (1)	?	1854.	49.1	6.8	J–T
pharmaceutical (2)	?	4100.	< 32.	2.9	J–T
paper(unbleached kraft)	6000.	142.	26.3/63.5 (GC)[2]	4.4/8.33(GC)	J–T
paper, tissue, plywood	42000.	136.	24.5/66.8 (GC)	8.5 (GC)	J–T
food, margarine, shortening	200.	236.	22.8	5.4	J–T
fibers, chemicals and plastics	12000.	452.	35.8	12.9	J–T
petroleum, refined pet. products	20000.	110.	58.0/87 (GC)	10.7/20.6 (GC)	J–T
petrochemical, 1,3 butadiene	2000.	94.	50.6	41.6	J–T
petrochemical, 1,2 di-chloroethane	432.	92.	57.5	25.1	J–T
petrochemical, 1,2 di-chloroethane	diluted 2:1	60.6	58.7	31.0	J–T
paper(bleached) pulp & kraft paper	22000.	311.	93.5	5.8	J–T

1 Jones–Thibodeaux this project work.

2 As per gas chromatograph analysis.

TABLE 7

Published Air-Volatile Fraction Data

Industry Type, Major Product	Wastewater Flow 1000 ga/da	Raw Conc.[4] mg/l	Volatile[4] Fraction %	Relative Vol. Rate K/a	Source
paper, pulp and kraft paper	1080.	72 –8390(BOD)	53–94(BOD)[3]	8–9	Estridge (1971)
pulp, cellulose	?	?	> 57(BOD)	–	Thibodeaux (1970)
unknown, styrene	?	?	~ 75(BOD)	–	Hiser (1970)
synthetic fiber, dacron	?	?	85(BOD)	–	Keen (Private Comm.)
petrochemical, vinyl chloride	504.	1200.	> 8.1	–	Minott (1973)
simulated, six components	–	–	91(GC)	17.0	J–T
domestic, Fayetteville, Ark.	*TOC SAMPLES CONTAMINATED* - - - - - - - - - - - - - - - -				J–T
domestic, Springdale, Ark.	6000.	254.	35.3	14.7	J–T

[3] Evap. condensates 74 & 88%, decker filtrate 53%, turpentine decanter underflow 94%.

[4] Total organic carbon unless specified otherwise.

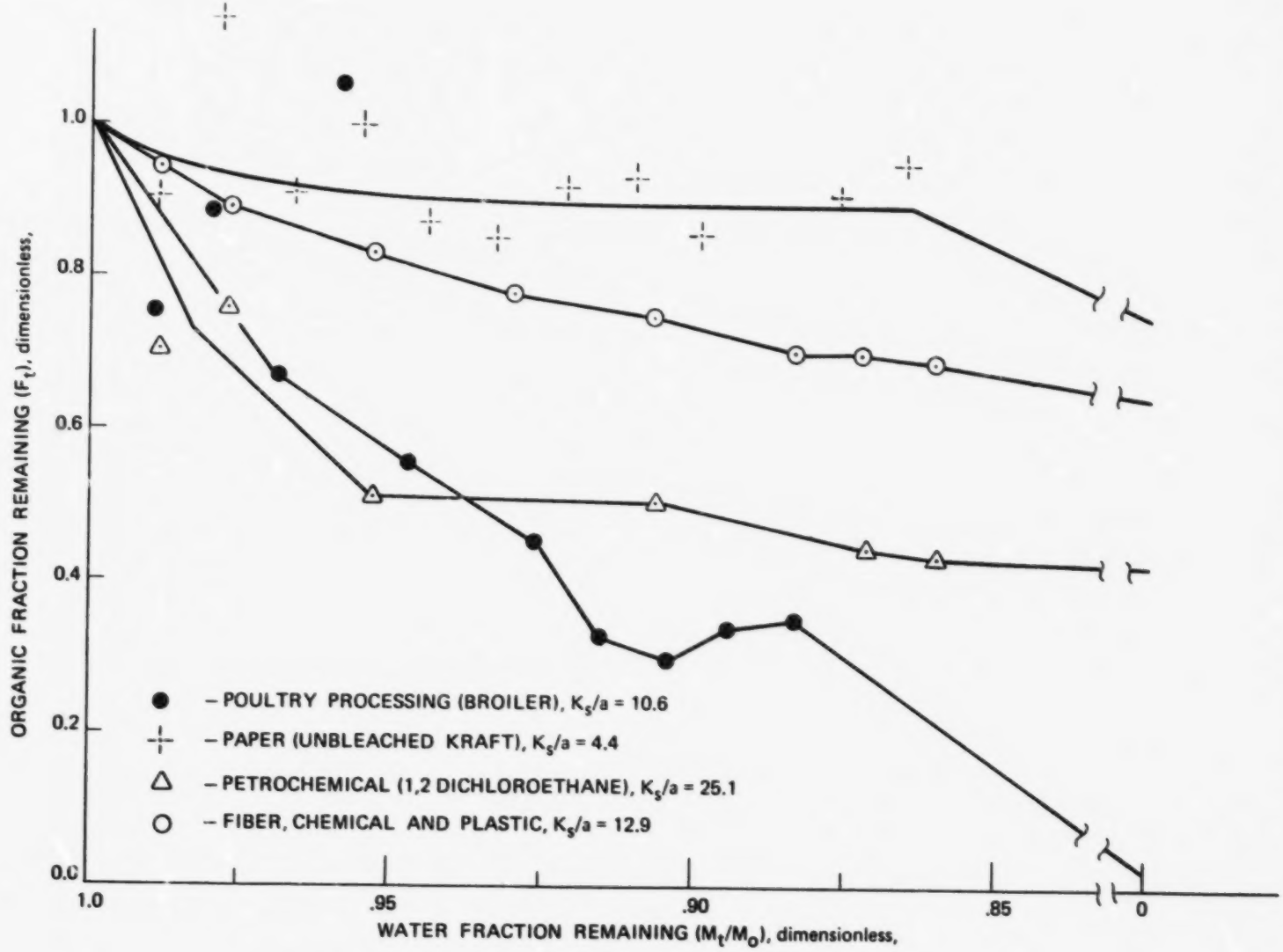


Figure 21. Desorption results for industrial wastewater -- I.

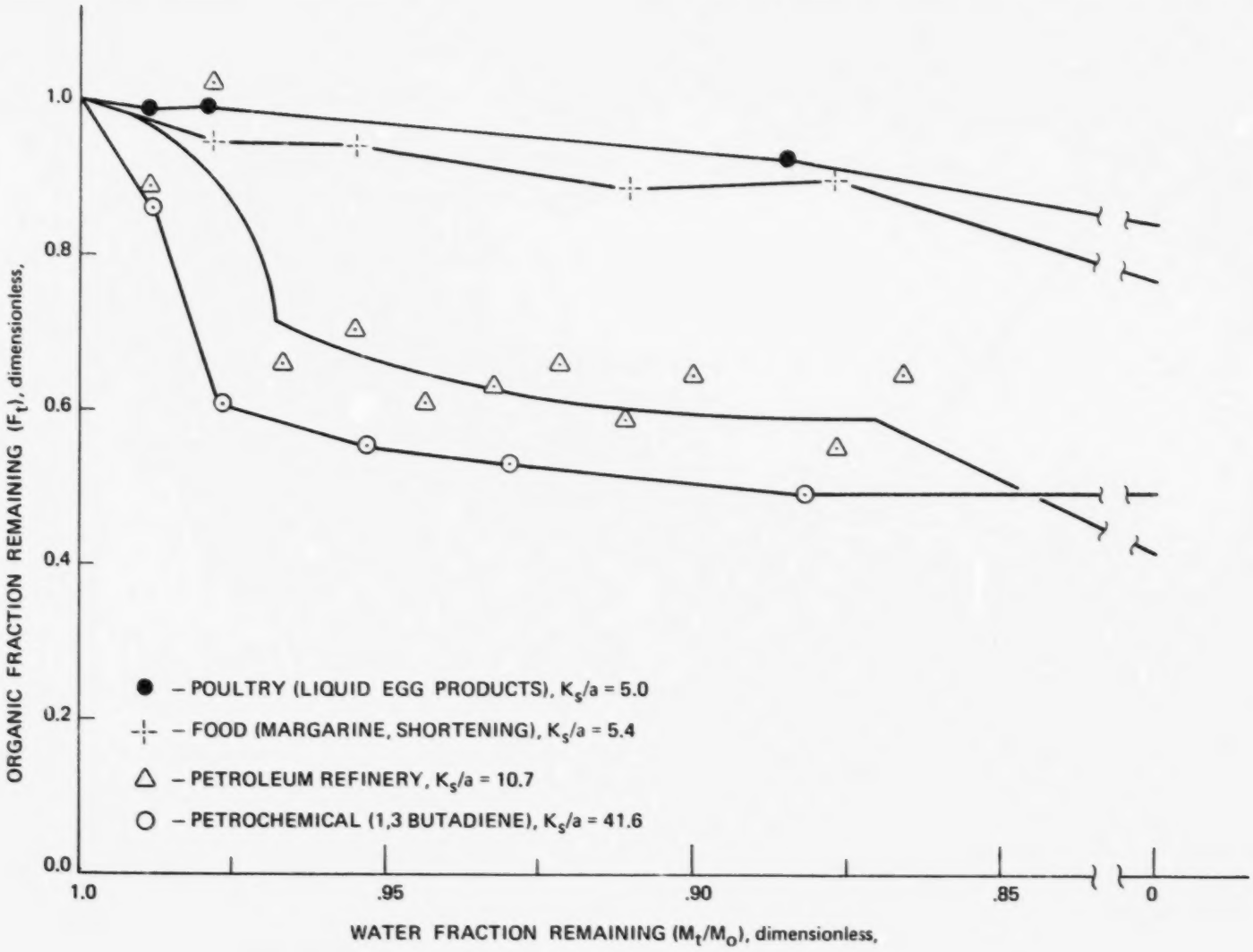


Figure 22. Desorption results for industrial wastewater – II.

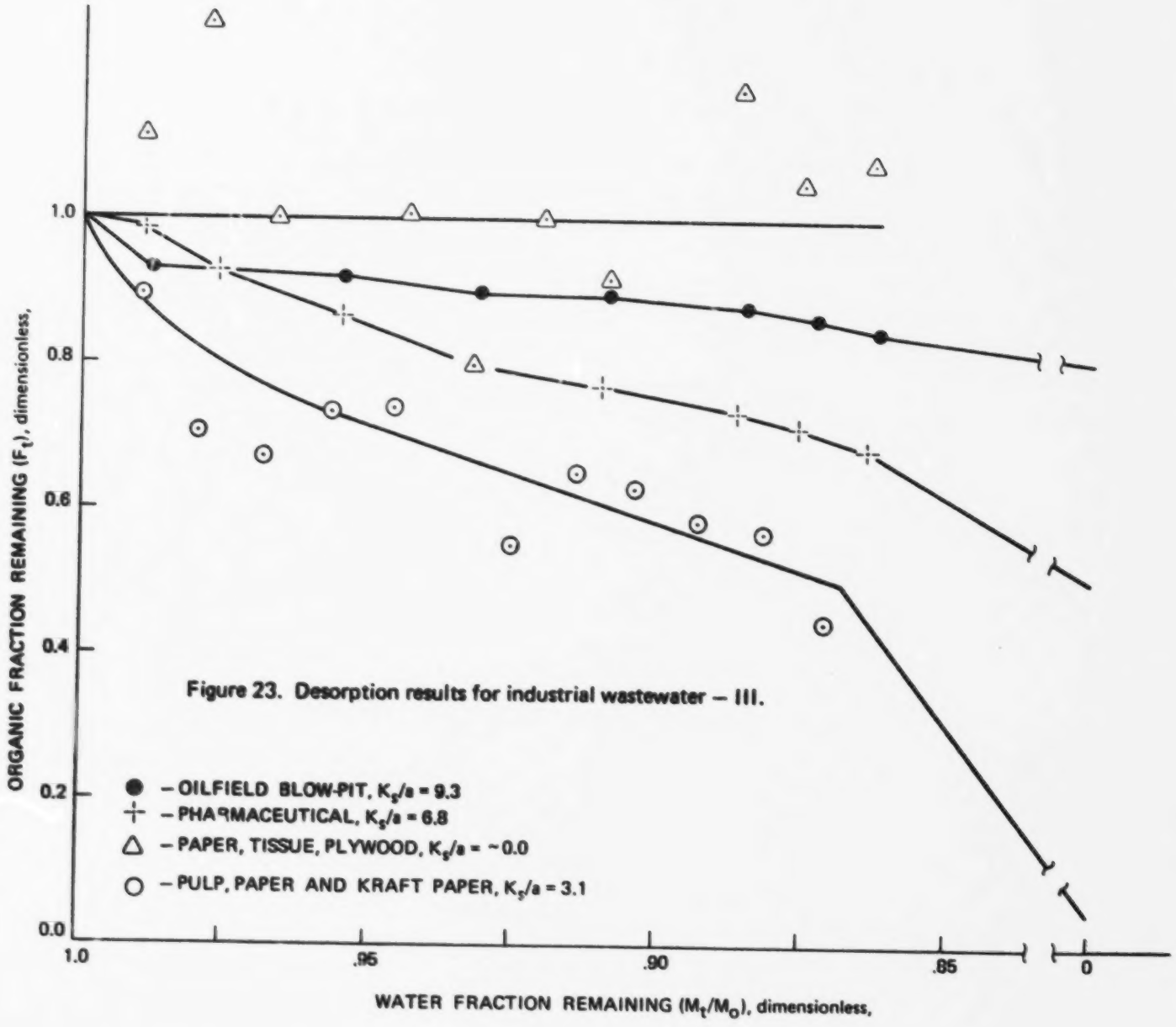


Figure 23. Desorption results for industrial wastewater – III.

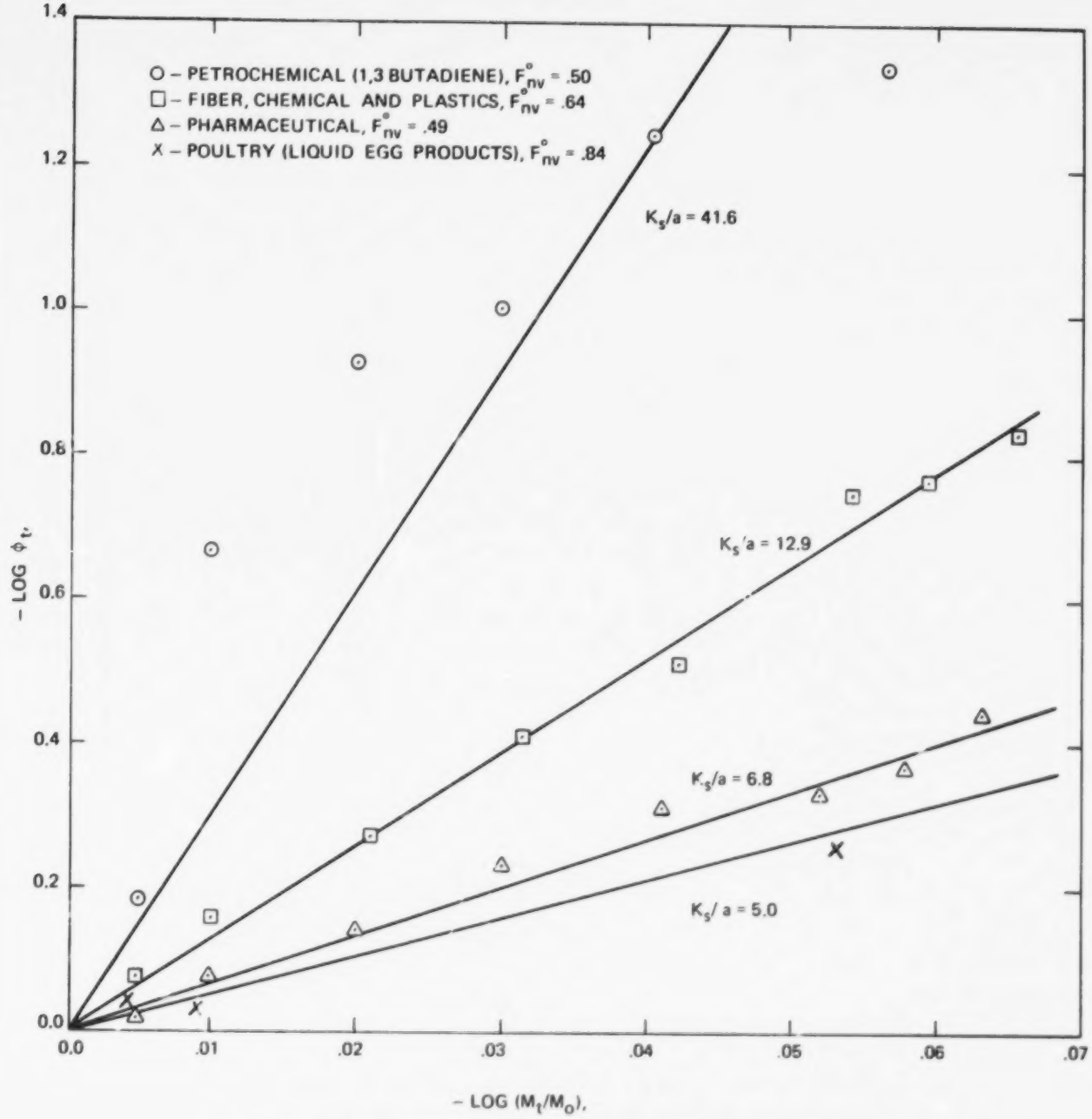


Figure 24. Relative volatilization rates of industrial wastewaters.

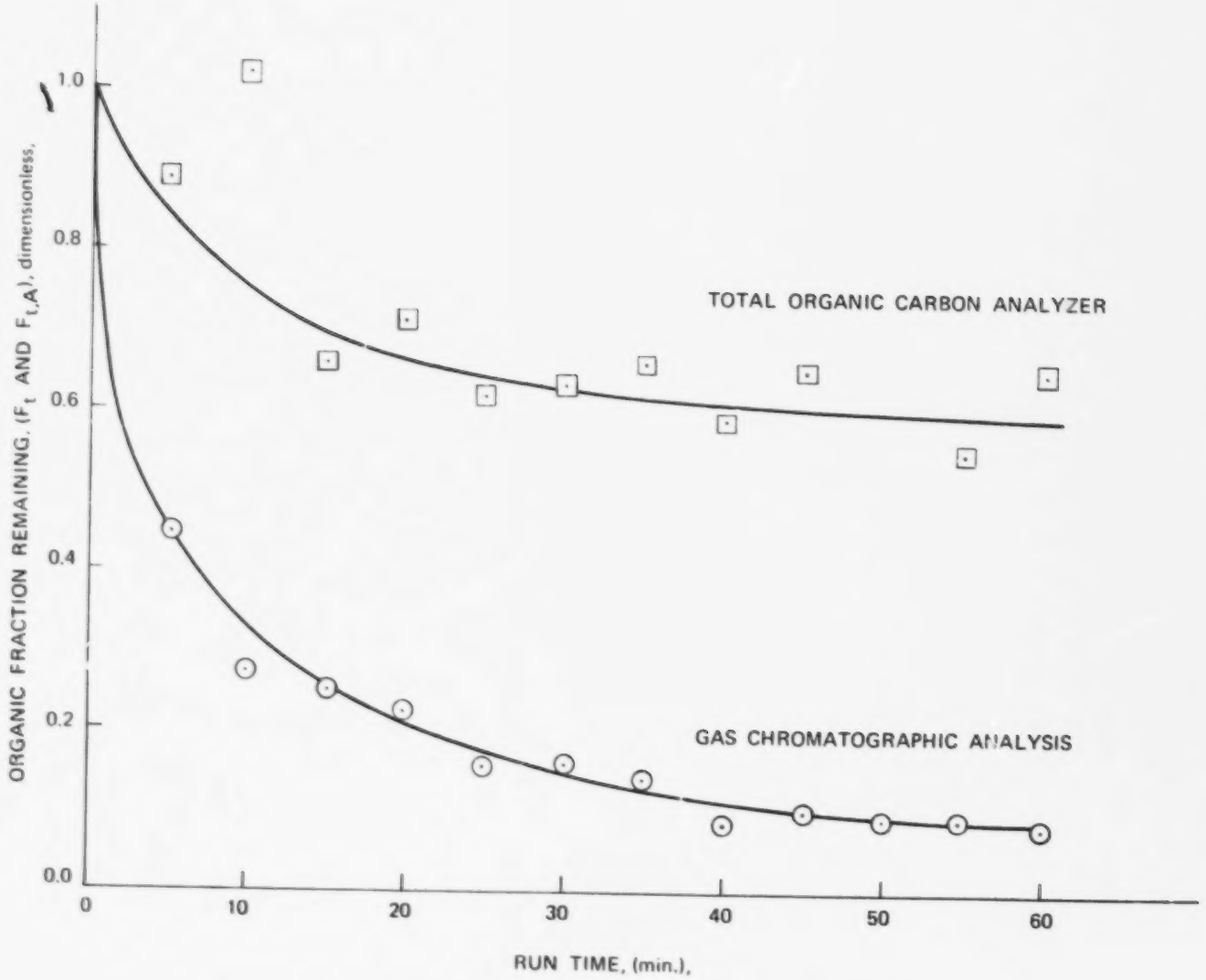


Figure 25. Petroleum refinery wastewater – T O C and G C results.

SECTION VIII

DISCUSSION

Experiments with pure components established that a batch recirculating packed column with countercurrent air flow can be an effective desorption device. Good comparison of experimental data with theoretical equations and calculated values instilled a degree of confidence in the analytical model developed for the desorption apparatus. Table 4 shows the extent to which the experimental results agree with the analytical model for the Raschig Ring apparatus.

The experimental results of tests run with pure components appear in Table 4. The data is tabulated in order of decreasing relative volatility and the experimental K/a values display this same decreasing trend. There is general quantitative agreement on K/a results between the various test methods. The data treatment techniques (i.e., slope from a log-log plot) is sensitive to errors in the test methods and may account for the relative wide range of K/a values. Figures 6 and 7 show that the least square algorithm will yield biased results if some data are in strong deviation from the trend. Ideally all test methods should yield identical experimental values of K/a for pure components.

Although the Raschig Ring apparatus displayed sizable errors in water loss, which will in turn effect K/a, there are instances of agreement between test methods worth noting in Table 4. The acetaldehyde results show good agreement between test methods. The BOD_5, COD and GC results for acetone (run 2) and methanol (run 1) are in fair agreement. All four test results for methanol (run 2) are in fair agreement. The results of both phenol runs are exceptionally good. Phenol has approximately the same relative volatilization rate as water and all six test results indicate this with a high degree of *absolute* accuracy. Considering the sensitivity of the log-log correlation to experimental test error it is doubtful that the most error free data will yield a K/a value with a range of uncertainty less than ± 1. K/a unit.

The agreement between repetitive runs for the Raschig Ring column is generally poor. The GC data for acetone in Table 4 is in fair agreement. The COD data for methanol is in good agreement. The phenol data is good in an absolute sense.

Statistical results (Table 5) of pure component experiments with the Raschig Ring column for K/a reveal that no test method emerges as being superior, however the standard error is usually less for the TOC and COD tests. Non-zero (with 95% confidence) K/a values were observed for methanol, acetone, acetaldehyde, n-butanol and i-butanol. K/a values not significantly different from zero were observed for phenol, acetic acid, formic acid and propionic acid. This is in general agreement with the theoretical K/a column of Table 4. An exhaustive set of experiments was not carried out with the Intalox Saddle device. **Recommended Test** – An Intalox Saddle device was developed (Figure 5) that displayed the same experimental behavior as the Raschig Ring device. This modified apparatus required

less sample, a shorter run time, was simpler to operate and gave considerably more accurate results. Water evaporation in a one hour run averaged 40.4 grams with a range of 38.4 to 42.4 grams for a percentage deviation range of −5.0% to 5.0%. The correspondence of repetitive runs with n-butanol (shown in Figure 13) is indicative of the reproducibility of the Intalox Saddle device results.

Experiments with selected pure chemicals revealed some information about desorption of solutions containing both volatile and non-volatile components. Desorption of simulated wastewater revealed that the non-volatile fraction remains in the aqueous phase and a volatile fraction is stripped out by the air (see Figure 10, 11 and 12). These simulated wastewater runs further suggest that the volatile fraction observed depends upon the test method. For example "Simulated Wastewater No. 2" (Figure 11) was found to contain a 50% volatile BOD_5 fraction, a 55% volatile COD fraction and a 65% volatile TOC fraction.

The gas-chromatograph should not be used to measure the volatile fraction in wastewater samples suspected to contain high molecular weight, non-volatile components. Figure 25 shows that gross errors can be made by attempting to use the G C for estimating the volatile fraction. The high molecular weight species are adsorbed strongly by the column and may never reach the detector. The volatile G C fraction may be 100% in most cases since it is typically the low molecular weight components that are selectively adsorbed and desorbed.

Results of the analytical model study reveal that the desorption experiment K/a result is sensitive to some operating parameters and insensitive to others. Column temperature and inlet air relative humidity should be controlled as accurately as possible (25°C ± 1°C and 0% R H). Moderate variations in the gas and liquid rate will have little effect on K/a. The desorption column should have a packed section $H_{OG,i}$ (height of transfer unit) equivalent to or greater than 15 cm. of .318 cm. (1/8 inch) Intalox Saddles. The ultimate volatile fraction (i.e., F_v°) is not effected by column operating condition, however the minimum F_t observed will depend upon run time. Ideally F_v° cannot be measured experimentally despite the length of the run time. The rate of removal of a volatile component approaches zero but can never reach it.

Experiments with compounds known to interfere with the mass-transfer process reveal some effect on K/a particularly with cetyl alcohol. Since desorption experiments will be performed with the wastewater in the "as found" state, care should be taken to exclude these extraneous compounds from the apparatus operation.

Desorption experiments on actual industrial wastewater samples was the final test for the apparatus. Nineteen samples were tested and were found to contain a range of volatile fractions. Sixty minute runs yielded experimental volatile fractions (F_{60}) of 0% to 70%. Ultimate volatile TOC fractions (i.e., F_v°) ranged from 0% to 98%. Relative volatilization rates ranged from 4.4 to 41.6 based on TOC analysis (see Table 6). The widely scattered data for the paper industry samples is possibly due to fiber fines that cause high organic

concentrations to be measured on the total carbon analyzer. In general all the industrial sample results display a behavior predicted by Equation (14). Some samples contain volatiles which display low K/a values and a sixty minute run time is too short for accurately determining F_v°. The poultry sample in Figure 21 and the paper and pharmaceutical samples in Figure 23 are examples. Figure 24 shows that relatively consistant values of K_s/a can be obtained from a desorption experiment. This figure represents the results of only the most consistant data results. Plots of this type are possible only if the wastewater test methods are performed with extreme care and utmost accuracy. No operating problems were encountered with any of the experimental runs. Significant odor reduction was noted during the experiment.

The Intalox Saddle device as described above appears to be ideally suited to perform desorption studies on industrial wastewater samples. It has a number of inherent advantages over sparged vessel type devices and hollow fiber devices (see Appendix C). The foremost advantage is that it simulates the desorption (or stripping) process as it occurs in cooling towers. The main advantages of packed column desorption are:

a) the apparatus is simple and the elements are readily available
b) the operation is simple to control and the experiment run time is short
c) standard wastewater test methods can be employed with the experiment
d) data handling and interpretation require elementary graphical or mathematical techniques.
e) a correction is available for air with a humidity other than 0% R H
f) the results are somewhat insensitive to operating conditions (except for temperature)
g) samples that have a tendency to foam when contacted with air can be readily handled.

The main disadvantages of the packed column desorption device are:

a) column temperature must be maintained constant (i.e., at 25°C, cooling tower inlet temperature, etc.)
b) samples should be kept in a chilled state before and after desorption
c) run times of greater than one hour may be desirable on some samples

The apparatus design and the organic concentration test method are somewhat related. The TOC (instrumental) test is possibly the best technique for measuring F_v° and K_s/a due to the present accuracy of these devices. If COD or BOD is employed, relatively large samples will be required from the desorption apparatus. A large flask (~ 1 liter) should be employed. COD and BOD are both useful for measuring F_v° and K_s/a. The GC should *not* be employed for F_v° measurements. K_s/a measurements can possible be estimated from GC results.

One most important use of this device is the simulation of stripping of volatile components from wastewater in industrial size cooling towers. An experimental value of

K_s/a is obtained from the Intalox Saddle desorption device operated at the proposed inlet water temperature. This relative volatilization rate is employed with an equation developed by McAlister, Turner and Estridge (1) to obtain the percentage extent of treatment by stripping in a cooling tower. The equation is

$$R = \frac{(K_s/a)\, a_{CT}\, (1 + B/L)}{(K_s/a)\, a_{CT} + B/L} \qquad (24)$$

where R = percentage of treatment by stripping

a_{CT} = fraction of water loss in cooling tower

B = blowdown rate from tower basin, l./min.

L = water flow rate to tower, l./min.

SECTION IX

REFERENCES

1. McAlister, J.A., B.G. Turner, and R.B. Estridge. Treatment of Selected Internal Kraft Mill Wastes in a Cooling Tower. Environmental Protection Agency, Water Pollution Control Research Series. Publication Number 12040 EEK. August, 1971.

2. Prather, V. Advanced Treatment of Petroleum Refinery Wastewater by Autoxidation. Journal Water Pollution Control Federation. 42 (4): 596 – 603, April 1970.

3. Mohler, E.F., H.F. Elkin, and L.R. Kumnick. Experience with Reuse and Bio-oxidation of Refinery Wastewater in Cooling Tower Systems. Journal Water Pollution Control Federation. 36 (11): 1380 – 1392, November 1964.

4. Burns, O.B., Jr. and W.W. Eckenfelder, Jr. Aeration Improvement and the Adaptation of a Cooling Tower to an Activated Sludge Plant. TAPPI 48 (11):96A(1965). Pilot Plant Evaluation of Plastic Trickling Filters in Series with Activated Sludge. TAPPI 48 (1): 42 (1965).

5. Cohn, R.G. and Tonn, E.T., Use of a Cooling Tower in Black Liquor Evaporation. TAPPI 47 (3): 163A (1964).

6. Engelbrecht, R.S., A.F. Gaudy, Jr. and J.M. Cederstrand. Diffused Air Stripping of Volatile Waste Components from Petrochemical Wastes. Jo. W.P.C.F. 33 (2): 127 - 135 Feb., 1961.

7. Gaudy, A.F. Jr., R.S. Engelbrecht, and B.G. Turner. Stripping Kinetics of Volatile Components of Petrochemical Wastes. Jo. W.P.C.F. 33 (4) 382 – 392, April, 1961.

8. Gaudy, A.F., Jr., B.G. Turner and S. Pusztaszeri. Biological Treatment of Volatile Waste Components. Jo. W.P.C.F. 35 (1): 75 – 93, January, 1963.

9. Eckenfelder, W.W., Jr. Industrial Water Pollution Control. McGraw-Hill Book Company, New York, 1966, p. 82.

10. Hiser, L.L. Selecting a Wastewater Treatment Process. Chemical Engineering Nov. 30, 1970. p. 79.

11. Goswami, S.R., Treatment of Strippable and Nonstrippable Substrates by the Activated Sludge Process. Ph.D. Thesis, Oklahoma State University, 1969.

12. Thibodeaux, L.J. and D.G. Parker. Desorption of Selected Gases and Liquids from Aerated Basins. (Presented at 76th National Meeting American Institute Chemical Engineers. Tulsa, Oklahoma. March 10–13, 1974.) Paper No. 30d.

13. Horton, J.H., J.C. Corey and R.M. Wallace. Tritium Losses from Water Exposed to the Atmosphere. Environmental Science and Technology 5 (4): 388 – 343, April, 1971.

14. Mackay, D. and A.W. Wolkoff. Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to the Atmosphere. Environmental Science and Technology 7 (7) 611 – 614, July, 1973.

15. Weimer, W.C. and G.F. Lee. Method for the Storage of Samples for Dissolved Gas Analyses. Environmental Science and Technology 5 (11): 1136 – 1138, November, 1971.

16. Pierotti, G.J., C.H. Deal and E.L. Derr. Activity Coefficients and Molecular Structure. Industrial and Engineering Chemistry. 51 (1): 95–102, January, 1959.

17. Thibodeaux, L.J., R.B. Estridge and B.G. Turner. Measurement of the Relative Volatilization of the Water-Miscible Fractions in an Aqueous Effluent. New York, American Institute of Chemical Engineers, Symposium Series 124, Volume 68, 1972.

18. Treybal, R.E. Mass-Transfer Operations, 2nd Edition. McGraw-Hill Book Company, New York, 1968. p. 164–171.

19. Reinhardt, J.A. An Experimental Apparatus for Measurement of Volatile Components in Aqueous Phases. Thesis (M.S.), University of Arkansas, Fayetteville, 1972.

20. American Public Health Association, Standard Methods for the Examination of Water and Waste Water, 13th Edition, New York, APHA Inc., 1971.

21. Emory, S.F. The Effect of Surface Active Agents on Interfacial Convection. New York, American Institute of Chemical Engineers Student Bulletin, p. 37, 1972.

SECTION X

PUBLICATIONS AND PATENTS

Two pending publications have been written as a result of this study.

1. Jones, Jack Ray; "Air Stripping of Volatile Components in Industrial Wastewater" University of Arkansas, Thesis, May, 1974.

2. Thibodeaux, L.J. and Jones, J.R.; "A Desorption Test for Quantifying the Volatile Organics in Industrial Wastewater" (proposal accepted for presentation at AIChE Meeting, Salt Lake City, Utah, Aug., 1974)

No patents have been produced or applied for under this project.

SECTION XI

GLOSSARY OF SYMBOLS

FREQUENTLY USED ABBREVIATIONS

ac = alternating current
BOD_5 = biological oxygen demand (5-day, 20°C)
°C = degrees Celsius
cm = centimeters
COD = chemical oxygen demand, mgO_2/l.
da = day
Exp = experiment
EXP = exponent (e = 2.71828)
°F = degrees Fahrenheit
ft = feet
ga = gallons
G C = gas chromatograph
Hg = mercury
in = inches
l = liters
log = common logarithm (i.e., base ten)
m = meters
mg = milligrams
mgC/l = milligrams carbon per liter
mgO_2/l = milligrams oxygen per liter
min = minutes
ml = milliliters
n– = normal
PCB_s = polychlorinated biphenyls
pH = –log[hydrogen ion concentration in gram ions per liter]
ppm = parts per million
RH = relative humidity
SCF = standard cubic feet (i.e., ft^3 at 32°F. and 1 atmosphere)
STP = standard temperature and pressure (i.e., 0°C and 760 mmHg or 32°F and 1 atmosphere)
TOC = total organic carbon
v = volts
wrt = with respect to

% = percent

> = greater than

>>> = much greater than

~ = approximately

≃ = approximately equal

≡ = a definition

∞ = infinity

SYMBOLS

Roman

A = integrator area, cm^2.

a = fraction water lost in column (dimensionless), regression equation constant

B = blowdown rate from cooling tower, l./min.

b = regression equation slope

C = concentration of gross organic pollutant measures (i.e., BOD_5, COD, and TOC), mg/l.

CV = coefficient of variation (standard error ÷ mean)

E = experimental percent relative humidity, %

F = organic fraction ($0 < F < 1$), dimensionless

G = gas flow rate through column, (g-moles)/(min)(cm^2)

H = height of a transfer unit, cm.

K = fraction of a volatile component lost in column, dimensionless

K/a = relative volatilization rate of a volatile component wrt water, dimensionless

L = liquid flow rate through column, (g-moles)/(min)(cm^2) or (g-moles)/(min)

M = quantity of liquor, grams. ΔM = change in quantity of liquor, grams.

m = sample size, grams. Δm = individual sample size, grams.

n = number of samples

p = vapor pressure, torr. or mmHg.

R = removal of BOD, COD, TOC in a cooling tower as a fraction or as a percent of it in feed liquor.

S = stripping factor, dimensionless

SE = standard error of estimate of regression equation

t = time, min. or statistical t-value.

W = weight, grams

X = independent linear regression variable

x = mole fraction in liquid, dimensionless, liquid phase concentration (same dimensions as C but for single components)

Y = dependent linear regression variable
y = mole fraction in gas, dimensionless
Z = height of packed section of desorption column, cm.

Greek

α = relative volatility, dimensionless
γ = activity coefficient, dimensionless
ϕ = fraction of the original volatile fraction remaining, dimensionless

SUBSCRIPTS

CT = cooling tower
e = experimental
f = final
i = volatile component
ii = inlet concentration of component i
io = outlet concentration of component i
j = non-volatile component
jo = initial concentration
m = total number of non-volatile components or designates a molar quantity (i.e., moles)
n = total number of volatile components
nv = non-volatile
o = original or initial
OG = overall gas phase
R = ratio (i.e., stripping factor ratio)
s = a pseudo volatile component
T = tower or column
t = at time t (i.e., one of many sample times)
v = volatile
w = water
x = liquid phase

SUPERSCRIPTS

$\bar{o}$ = original or pure component
* = in equilibrium

SECTION XII

APPENDICES

		Page
A.	Raw Experimental Data	74
B.	Computer Program to Calculate F_v° and K_s/a for Industrial Wastewater Samples	119
C.	A Hollow Fiber Device as a Desorption Apparatus	126

APPENDIX A

RAW EXPERIMENTAL DATA

Experiment 1

component(s)	methanol-water
initial concentration	approx. 1000 ppm methanol in H_2O
initial charge volume	2876 ml
water vaporized	245 ml
liquid flow rate	700 ml/min (4,840 lbs/HR-ft^2)
gas flow rate	1.828 ft^3/min ΔP = 11" Hg
inlet dry bulb temperature of air	77 °F
inlet wet bulb temperature of air	68 °F
liquid temperature	68 °F

Time into Experiment	Analysis Concentrations			
	COD	GC	TOC	BOD
(min)	(ppm MeOH)	(ppm MeOH)	(ppm MeOH)	(ppm MeOH)
0	805	550	570	520
15	734	538	424	530
30	718	522	320	493
45	685	492	251	560
60	636	442	251	487
75	615	432	251	477
90	598	423	214	447
105	528	401	181	453
120	496	390	165	333
135	474	365	101	420
150	442	340	67	350
165	421	325	120	400
180	399	300	120	300
195	405	312	67	300

Experiment 2

components	methanol-water
initial concentration	approx 100 ppm methanol in water
initial charge volume	2913 ml.
water vaporized	245 ml.
liquid flow rate	700 ml/min. (4,840 lbs/HR-ft^2)
gas flow rate	1.828 ft^3/min.
inlet dry bulb temperature of air	78° F
inlet wet bulb temperature of air	66° F
liquid temperature	66° F

Time into Experiment	Analysis Concentrations			
	COD	GC	TOC	BOD
(min)	(ppm MeOH)	(ppm MeOH)	(ppm MeOH)	(ppm MeOH)
0	916	1030	414	580
15	826	970	395	510
30	787	925	347	440
45	723	842	347	410
60	686	812	288	460
75	632	820	288	340
90	611	595	288	340
105	630	710	248	330
120	563	630	237	280
135	546	610	206	220
150	499	560	197	260
165	493	512	206	220
180	429	470	181	180
195	434	438	160	200

Experiment 3

components	acetone-water
initial concentration	approx 1000 ppm acetone in water
initial charge volume	2912 ml
water vaporized	174 ml
liquid flow rate	700 ml/min (4,840 lbs/Hr-ft^2)
gas flow rate	1.828 ft^3/min
inlet dry bulb temperature	75° F
inlet wet bulb temperature	63° F
liquid temperature	63° F

Time into Experiment	Analysis Concentration (ppm ACETONE)			
(minutes)	COD	GC	TOC	BOD
0	1223	1000	861	554
15	734	866	515	412
30	470	410	298	256
45	258	281	185	142
60	179	160	106	106
75	111	108	0	62
90	89	68	0	31
105	11	83	0	27
120	14	0	0	10
135	0	0	0	3
150	11	0	0	2
165	0	0	0	2
180	0	0	0	0
195	0	0	0	2

Experiment 4

components	acetone-water
initial concentration	approx 1000 ppm Acetone in water
initial charge volume	3013 m.
water vaporized	268 ml
liquid flow rate	700 ml/min (4,840 lbs/Hr-ft^2)
air flow rate	1.828 ft^3/min
inlet dry bulb temperature	82° F
inlet wet bulb temperature	64° F
liquid temperature	64° F

Time into Experiment	Analysis Concentrations (ppm Acetone)			
(min)	COD	GC	TOC	BOD
0	757	940	563	353
15	433	545	245	126
30	225	300	145	149
45	133	210	56	85
60	79	145	24	51
75	55	85	8	41
90	0	100	3	34
105	14	0	3	24
120	0	0	0	24
135	14	0	0	7
150	12	0	0	17
165	18	0	0	17
180	11	0	0	7
195	11	0	0	14

Experiment 5

components	Phenol-water
initial concentration	approx 1000 ppm Phenol in water
initial charge volume	2937 ml
water vaporized	251 ml
liquid flow rate	700 ml/min
air flow rate	1.575 ft^3/min. 9.5" Hg
inlet dry bulb temperature	83° F
inlet wet bulb temperature	67° F
liquid temperature	67° F

Time into Experiment	Analysis Concentrations (ppm Phenol)			
(min.)	COD	GC	TOC	BOD
0	978		509	636
15	950		477	636
30	949		490	611
45	922		490	623
60	987		473	598
75	969		465	579
90	960		496	611
105	967		487	579
120	979		487	566
135	953		487	611
150	994		514	579
165	975		487	611
180	993		490	579
195	1002		509	578

Experiment 6

components	Phenol-water
initial concentration	approx 1000 ppm Phenol in water
initial charge volume	2855 ml
water vaporized	241 ml
liquid flow rate	700 ml/min
air flow rate	1.545 ft^3/min
inlet dry bulb temperature	80° F
inlet wet bulb temperature	67° F
liquid temperature	67° F

Time into Experiment	Analysis Concentrations (ppm Phenol)			
(min)	COD	GC	TOC	BOD
0	948		386	648
15	946		400	604
30	940		438	679
45	934		409	686
60	932		419	611
75	917		419	661
90	940		426	686
105	941		419	673
120	934		354	626
135	913		386	635
150	948		401	641
165	944		401	667
180	932		400	617
195	964		400	654

Experiment 7

components	Acetone-Phenol-Water
initial concentration	approx 500 ppm Acetone + 500 ppm Phenol in water
initial charge volume	3027 ml
water vaporized	215 ml
liquid flow rate	700 ml/min
air flow rate	1.828 ft^3/min
inlet dry bulb temperature	75° F
inlet wet bulb temperature	64° F
liquid temperature	64° F

Time into Experiment	Analysis Concentrations		
	COD	TOC	BOD
(min)	(ppm Oxygen)	(ppm C)	(ppm Oxygen)
0	2064	378	1450
15	1741	310	1275
30	1564	275	1080
45	1412	250	985
60	1332	253	955
75	1255	253	930
90	1259	250	890
105	1263	248	840
120	1340	238	860
135	1296	232	840
150	1244	225	865
165	1276	225	855
180	1292	200	825
195	1268	208	845

Experiment 8

components	Acetone, Phenol, Methanol, and Water
initial concentration	approx 333 ppm of each organic component in the water
initial volume charge	2980 ml
water vaporized	211 ml
liquid flow rate	700 ml/min
air flow rate	1.828 ft^3/min
inlet dry bulb temperature	74° F
inlet wet bulb temperature	63° F
liquid temperature	63° F

Time into Experiment	Analysis Concentrations		
	COD	TOC	BOD
(min)	(ppm oxygen)	(ppm carbon)	(ppm oxygen)
0	2032	350	1380
15	1650	670	1155
30	1521	590	1020
45	1385	570	915
60	1304	545	900
75	1242	470	795
90	1187	451	810
105	1022	435	795
120	1007	396	765
135	960	355	720
150	934	375	680
165	920	330	675
180	917	330	675
195	923	305	705

Experiment 9

components	Acetone, Phenol, Methanol, and Water
initial concentration	approx 333 ppm of each organic compond in water
initial volume charge	2970 ml
water vaporized	134 ml
liquid flow rate	700 ml/min
air flow rate	1.828 ft^3/min
inlet dry bulb temperature	78° F
inlet wet bulb temperature	68° F
liquid temperature	68° F

Time into Experiment	Analysis Concentration	
	COD	BOD
(min)	(ppm oxygen)	(ppm oxygen)
0	1948	1350
5	1813	1250
10	1695	1140
15	1498	1050
20	1446	960
25	1430	930
30	1332	810
35	1338	870
40	1298	750
45	1267	810
50	1184	750
55	1197	750
60	1179	690
65	1138	690
70	1135	720
75	1161	780
80	1100	660
85	1075	630
90	1104	810

Experiment 1-18-73

components	formic acid - water
initial concentration	approx 1000 ppm
initial volume charge	3500 ml
water vaporized	223 ml
liquid flow rate	610 ml/min
air flow rate	1.65 ft^3/min
inlet air humidity	less than 30%

Time into Experiment		Analysis Concentrations		
	TEMP	COD	TOC	BOD
(min)	(F^o)	(ppm O_2)	(ppm C)	(ppm O_2)
0	68	—	967.7	—
15	66	—	652.0	—
30	66	—	757.0	—
45	64	—	767.0	—
60	64	—	748.0	—

Experiment 2-26-73

components	acetic acid - water
initial concentration	approx 1000 ppm
initial volume charge	3367 ml
water vaporized	233 ml
liquid flow rate	570 ml/min
air flow rate	1.65 ft^3/min
inlet air humidity	less than 30%

Time into Experiment		Analysis Concentrations		
	TEMP	COD	TOC	BOD
(min)	(F^o)	(ppm O_2)	(ppm C)	(ppm O_2)
0	77	1223.0	950.0	1410
15	68.5	1079.3	787.5	1305
30	68	1092.4	850.0	1305
45	65.5	1076.7	837.5	1335
60	64	1063.6	837.5	1350
75	63	1208.1	775.0	1335
90	63	1120.9	787.5	1260
105	63	1178.0	812.5	1290
120	63	1064.4	800.0	1200
135	63	1131.3	800.0	1065
150	63	1157.2	806.3	1080
165	63	1131.3	800.0	1125
180	63	1120.9	800.0	1065

Experiment 3-8-73

components	propionic acid - water
initial concentration	approx 1000 ppm
initial volume charge	3723 ml
water vaporized	348 ml
liquid flow rate	570 ml/min
air flow rate	1.65 ft^3/min
inlet air humidity	less than 30%

Time into Experiment		Analysis Concentrations		
	TEMP	COD	TOC	BOD
(min)	(F°)	(ppm O_2)	(ppm C)	(ppm O_2)
0	75	1149.1	662.9	960
15	70	1210.8	713.7	810
30	68	1287.9	858.2	990
45	67	1318.8	713.7	1020
60	66	1365.0	745.1	810
90	66	1324.3	796.5	735
120	66	1279.7	750.3	990
150	66	1309.4	765.3	975
180	66	1354.1	755.4	810

Experiment 3-23-73

compeonents	acetaldehyde - water
initial concentration	approx 1000 ppm
initial volume charge	3501 ml
water vaporized	260 ml
liquid flow rate	570 ml/min
air flow rate	1.65 ft^3/min
inlet air humidity	less than 30%

Time into Experiment		Analysis Concentrations		
	Temp	COD	TOC	BOD
(min)	(F^o)	(ppm O_2)	(ppm C)	(ppm O_2)
0	75	1467.8	599.5	1050
3	74	1287.4	462.0	810
6	72	1139.8	416.2	690
9	72	992.2	397.8	630
12	71	844.6	297.0	450
15	70	721.6	242.0	510
20	69	590.4	150.3	630
25	68	475.6	141.2	330
30	68	377.2	95.3	30

Experiment 4-13-73

components	propanol - water
initial concentration	approx 1000 ppm
initial volume charge	3341 ml
water vaporized	237 ml
liquid flow rate	540 ml/min
air flow rate	1.65 ft^3/min
inlet air humidity	less than 30%

Time into Experiment		Analysis Concentrations		
	TEMP	COD	TOC	BOD
(min)	(F^o)	(ppm O_2)	(ppm C)	(ppm O_2)
0	72	1822.2	663	1125
5	68	1802.2	600	1035
10	68	1762.1	567	1095
15	67	1722.1	617	1035
25	67	1642.0	583	975
35	66.5	1533.5	517	975
45	66	1441.7	517	960
60	66	1261.5	467	900
75	66	1121.3	457	840
90	66	1061.3	417	795
105	66	980.0	400	705
120	66	920.0	317	570
135	66	860.0	333	375
150	66	760.0	317	330
165	66	720.0	200	270
180	66	720.0	267	180

Experiment 4-18-73

components	isopropanol - water
initial concentration	approx 1000 ppm
initial volume charge	3546 ml
water vaporized	211 ml
liquid flow rate	540 ml/min
air flow rate	1.65 ft^3/min
inlet air humidity	less than 30%

Time into Experiment		Analysis Concentrations		
	TEMP	COD	TOC	BOD
(min)	(F°)	(ppm O_2)	(ppm C)	(ppm O_2)
0	80	1860.0	617	150
5	—	1580.0	600	60
10	74	1520.0	550	150
15	72	1380.0	500	60
25	70	1394.0	533	90
35	68	1316.5	500	90
45	68	1220.0	667	60
60	67	1142.2	467	150
75	66	1006.7	450	90
90	66	1232.4	350	60
105	66	1175.5	330	60
120	66	1175.5	300	90
135	66	1099.7	267	60
150	66	1080.7	317	60
165	66	777.4	250	90
180	66	815.3	317	150

Experiment 6-1-73

components	sucrose - water
initial concentration	approx 2000 ppm
initial volume charge	3612 ml
water vaporized	942 ml
liquid flow rate	540 ml/min
air flow rate	1.65 ft^3/min
inlet air humidity	less than 30%

Time into Experiment		Analysis Concentrations		
	TEMP	COD	TOC	BOD
(min)	(F^o)	(ppm O_2)	(ppm C)	(ppm O_2)
0	72	——	1780	——
30	69	——	1800	——
60	68	——	1800	——
90	68	——	1870	——
120	68	——	——	——
150	68	——	1950	——
180	68	——	1820	——
210	68	——	2040	——
240	66	——	2100	——
270	66	——	2020	——
300	66	——	——	——
330	66	——	1970	——
360	66	——	——	——
390	66	——	2040	——
420	66	——	2040	——
420	74	——	2120	——
450	68	——	2230	——
480	66	——	2190	——
510	66	——	2210	——
540	66	——	2380	——
570	66	——	——	——
587	66	——	2210	——

Experiment 7-17-73

industry	poultry - broiler processing
initial concentration	pure waste
initial weight charge	300 gm
water vaporized	41.1 gm
liquid flow rate	112 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
0	3037
5	2837
10	3060
15	3200
20	—
25	—
30	—
35	—
40	—
45	—
50	—
55	—
60	3670

Experiment 7-18-73

industry	metal - forge and plating
initial concentration	pure waste
initial weight charge	300 gm
water vaporized	38.7 gm
liquid flow rate	125 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
C	367
60	378

Experiment 7-19-73

industry	food - grape products
initial concentration	pure waste
initial weight charge	300 gm
water vaporized	38.5 gm
liquid flow rate	122 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment	Analysis Concentrations
	TOC
(minutes)	(ppm Carbon)
0	665
60	722

Experiment 7-23-73

industry	poultry - liquid egg products
initial concentration	pure waste
initial weight charge	300 gm
water vaporized	37.2 gm
liquid flow rate	112 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25 °C

Time into Experiment (min)	Analysis Concentrations TOC (ppm Carbon)
0	1545
5	1540
10	1560
15	—
20	—
25	—
30	—
35	—
40	—
45	—
50	—
55	—
60	1620

Experiment 7-31-73

components	styrene - water
initial concentration	approx 1000 ppm
initial weight charge	300.3 gm
water vaporized	10.6 gm
liquid flow rate	129.5 ml/min
air flow rate	0.6 ft^3/min
dry aid	air bottle
liquid temperature	25° C

Time into Experiment	Analysis Concentrations
	TOC
(seconds)	(ppm Carbon)
0	76
45	—
90	137
150	111
210	169
285	65
360	147
435	455
530	41
590	24
660	325
720	—
780	—
840	—
900	—
960	—

Experiment 8-1-73

components	benzene - water
initial concentration	approx 1000 ppm
initial weight charge	300.3 gm
water vaporized	10.4 gm
liquid flow rate	141 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
0	640
1	—
2	336
3	169
4	201
5	57
6	27.4
7	141
8	—
9	51
10	55
11	97
12	—
13	38
14	--
15	—

Experiment 8-16-73

components	sucrose, phenol, acetone, acetaldehyde, styrene, n-butanol, acetic acid, water
initial concentrations	50 μl of each component
initial weight charge	303.5 gm
water vaporized	42.3 gm
liquid flow rate	144 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25 °C

Time into Experiment	Analysis Concentrations
	GC
(min)	(average weight, gm)
0	0.018
5	0.013
10	0.011
15	0.008
20	0.009
25	0.008
30	0.008
35	0.009
40	0.009
46	0.009
50	0.011
55	0.009
60	0.012

Experiment 8-22-73

industry	poultry - broiler processing
intital concentration	pure waste
initial weight charge	300 gm
water vaporized	37.8 gm
liquid flow rate	129 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
0	—
5	122
10	93
15	111
20	84.5
25	135
30	72
35	—
40	60
45	44
50	40
55	47
60	49

Experiment 8-23-73

industry	poultry - broiler processing
initial concentration	pure waste
initial weight charge	300 gm
water vaporized	41.7 gm
liquid flow rate	153 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25 °C

Time into Experiment	Analysis Concentrations
	TOC
(min)	(ppm Carbon)
0	80
5	62
10	78
15	—
20	—
25	91
30	93
35	87
40	109
45	—
50	82
55	98
60	96

Experiment 8-24-73

components	ammonium chloride, sodium hydroxide, water
initial concentration	ph. 11
initial weight charge	301.3 gm
water vaporized	39.5 gm
liquid flow rate	128 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations Spectrophotometer (ppm ammonia)
0	—
3	—
6	—
9	—
12	880
15	868
20	852
25	825
30	788
35	735
40	710
45	630
50	481
55	452
60	—

Experiment 8-28-73

components	sucrose - water
initial concentration	approx 2000 ppm
initial weight charge	300.6 gm
water vaporized	138 gm
liquid flow rate	138 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
0	—
15	1210
33	—
45	1310
60	1360
75	—
90	1460
105	1520
120	1640
135	1640
150	1730
165	1790
180	1910

Experiment 9-10-73

Industry	paper - pulp, unbleached kraft paper
initial concentration	pure waste
initial weight charge	300.1 gm
water vaporized	38.6 gm
liquid flow rate	132 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment	Analysis Concentration	
	TOC	GC
(minutes)	(ppm Carbon)	(average weight, grams)
0	311	0.027
5	282	0.021
10	224	0.021
15	216	0.020
20	238	0.019
25	244	0.017
30	296	0.016
35	187	0.014
40	222	0.012
45	218	0.012
50	240	0.011
55	187	—
60	158	—

Experiment 9-11-73

industry	paper - unbleached kraft paper
initial concentration	pure waste
initial weight charge	300 gm
water vaporized	40.5 gm
liquid flow rate	132 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations GC (average area, grams)
0	0.018
5	0.018
10	0.016
15	0.017
20	0.016
25	0.015
30	0.015
35	0.020
40	0.018
45	0.019
50	0.018
55	0.015
60	0.015

Experiment 9-13-73

industry	food - shortening & margerine
initial concentration	87.3 gm pure waste
initial weight charge	300.4 gm
water vaporized	40.2 gm
liquid flow rate	147 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentration GC (average heights, units)
0	96
5	85
10	82
15	79
20	70
25	68
30	54
35	53
40	47
45	44
50	42
55	40
60	40

Experiment 9-17-73

industry	paper - tissue, paper, & plywood
initial concentration	pure waste
initial weight charge	300.2 gm
water vaporized	41 gm
liquid flow rate	154 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment	Analysis Concentrations	
	TOC	GC
(minutes)	(ppm Carbon)	(average area, units)
0	173	0.020
5	73	0.018
10	162	0.015
15	195	0.014
20	—	0.013
25	—	0.012
30	224	0.012
35	156	0.011
40	167	0.010
45	124	0.010
50	396	0.008
55	238	0.007
60	198	0.007

Experiment 10-29-73

industry	petroleum - refined petroleum products
initial concentration	pure waste
initial weight charge	300 gm
water vaporized	40.1 gm
liquid flow rate	136 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment	Analysis Concentrations	
	TOC	GC
(minutes)	(ppm Carbon)	(average height, cm.)
0	74	7.63
5	79	5.07
10	96	4.23
15	60	5.77
20	68	6.10
25	—	4.73
30	—	5.67
35	—	5.60
40	—	3.78
45	—	4.50
50	—	4.60
55	54	5.30
60	69	5.20

Experiment 12-18-73

industry	petrochemical - fibers, chemicals, & plastics
initial concentration	pure waste
initial weight charge	300 gm
water vaporized	42 gm
liquid flow rate	143 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
0	464
5	430
10	413
15	—
20	393
25	—
30	380
35	—
40	374
45	—
50	362
55	364
60	368

Experiment 12-21-73

industry	petrochemical - 1,3 butadiene
initial concentrations	185 gm pure waste
initial weight charge	300 gm
water vaporized	42 gm
liquid flow rate	138 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
0	58
5	50
10	36
15	—
20	34
25	—
30	34
35	—
40	33
45	—
50	51
55	44
60	33
	—

Experiment 12-27-73

components	n-butanol - water
initial concentration	approx 1000 ppm
initial weight charge	300.3 gm
water vaporized	40.6 gm
liquid flow rate	144 ml/min
air flow rate	0.6 ft^3/min
dry air	dry air
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
0	302
5	266
10	216
15	—
20	—
25	—
30	—
35	—
40	156
45	—
50	120
55	116
60	94

Experiment 1-2-74

industry	petrochemical - 1,2 dichloroethane
initial concentration	920.7 gm pure waste
initial weight charge	300.4 gm
water vaporized	40 gm
liquid flow rate	156 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
0	60.6
5	48.9
10	33.5
15	—
20	30.6
25	—
30	30.4
35	—
40	29.7
45	—
50	28.8
55	30.4
60	34.1

Experiment 1-16-74

industry	pharmaceutical waste (?)
initial concentration	pure waste
initial weight charge	300.7 gm
water vaporized	40.7 gm
liquid flow rate	123 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
0	1854
5	1846
10	1760
15	—
20	1680
25	—
30	1586
35	—
40	1564
45	—
50	1538
55	1516
60	1470

Experiment 1-18-74

industry	oilfield - natural gas blow pit waste
initial concentration	pure waste
initial weight charge	300 gm
water vaporized	41.5 gm
liquid flow rate	130 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
0	102.4
5	96.4
10	97.2
15	—
20	98.6
25	—
30	99.0
35	—
40	101.4
45	—
50	102.0
55	101.4
60	100.6

Experiment 1-20-74

components	n-butanol - water
initial concentration	approx 1000 ppm
initial weight charge	300.6 gm
water vaporized	46.6 gm
liquid flow rate	144 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25 °C

Time into Experiment	Analysis Concentrations
	TOC
(min)	(ppm Carbon)
0	388
5	302
10	268
20	224
30	190
40	156
50	130
55	112
60	96

Experiment 1-21-74

components	n-butanol - water
initial concentration	approx 1000 ppm
initial weight charge	300.3 gm
water vaporized	42.5 gm
liquid flow rate	152 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25° C

Time into Experiment (minutes)	Analysis Concentrations TOC (ppm Carbon)
0	374
5	352
10	324
15	—
20	264
25	—
30	216
35	—
40	180
45	—
50	142
55	125
60	110

Experiment 1-22-74

concentrations	n-butanol - water
initial concentration	approx 1000 ppm
initial weight charge	300.3 gm
water vaporized	54.1 gm
liquid flow rate	158 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25 °C

Time into Experiment (min)	Analysis Concentrations TOC (ppm Carbon)
0	396
5	358
10	328
20	284
30	258
40	210
50	178
55	144
60	108

Experiment 1-25-74

components	n-butanol - acetyl alcohol - water
initial concentration	approx 1000 ppm (n-butanol) 50 ppm (acetyl alcohol)
initial weight charge	300.3 gm
water vaporized	40.6 gm
liquid flow rate	154 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25 °C

Time into Experiment (min)	Analysis Concentrations TOC (ppm Carbon)
0	342
5	370
10	338
20	266
30	250
40	216
50	188
55	160
60	150

Experiment 1-28-74

components	n-butanol - water - sodium tetradecyl sulfate
initial concentration	approx 1000 ppm ($n-C_4H_9OH$) 50 ppm (NaTDS)
initial weight charge	300.7 gm
water vaporized	40.1 gm
liquid flow rate	156 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25 °C

Time into Experiment (min)	Analysis Concentrations TOC (ppm Carbon)
0	398
5.5	366
10	352
20	300
30	254
40	220
50	180
55	172
60	156

Experiment 1-29-74

components	n-butanol - water - sodium phosphate - dibasic heptahydrate
initial concentration	approx 1000 ppm ($n-C_4H_9OH$), 10 μl (sodium phosphate), 10 μl (DB HHD)
initial weight charge	300.3 gm
water vaporized	40.1 gm
liquid flow rate	154 ml/min
air flow rate	0.6 ft^3/min
dry air	air bottle
liquid temperature	25 °C

Time into Experiment (min)	Analysis Concentrations TOC (ppm Carbon)
0	374
5	360
10	338
20	288
30	236
40	222
50	168
55	166
60	146

APPENDIX B

COMPUTER PROGRAM TO CALCULATE F_v° AND K_s/a

FOR INDUSTRIAL WASTEWATER SAMPLES

Reproduced from
best available copy.

```
$JOB          WATSTV
C      E.P.A. 3-801376
C*****************************************
C
C                    OBJECTIVE OF PROGRAM
C
C         THIS PROGRAM COMPUTES THE ULTIMATE NON-VOLATILE ORGANIC
C      OR INORGANIC FRACTION(I.E., F = TIME INFINITY) AND THE REL-
C      ATIVE VOLATILIZATION RATE(I.E. K/A) FROM EXPERIMENTAL DATA
C      OBTAINED FROM A DESORPTION EXPERIMENT WITH A SAMPLE OF
C       INDUSTRIAL OR DOMESTIC WASTEWATER.
C           F=THE ULTIMATE(I.E., MAXIMUM) NON-VOLATILE FRACTION.
C          THE VOLATILE FRACTION MAY BE OBTAINED BY SUBTRACTING
C          F FROM UNITY.  THE VOLATILE FRACTION IS THE ULTIMATE
C          QUANTITY OF THE ORGANIC OR INORGANIC CONSTITUENTS IN THE
C          WASTEWATER THAT CAN BE TRANSFERRED TO THE AIR BY STRIPPING.
C          IT IS ALSO TRANSFERRED TO THE AIR IN ANY OPERATION THAT
C          INVOLVES CONTACTING THE WASTEWATER WITH AIR (I.E., ACT-
C          IVATED SLUDGE, TRICKLING FILTERS, AERATED STABILIZATION
C          BASINS, COOLING TOWERS, ETC.)
C           K/A= THE RELATIVE VOLATILIZATION RATE.  THIS PARAMETER
C          IS THE RATIO OF THE RATE OF DESORPTION OF THE ORGANIC
C          OR INORGANIC CONSTITUENT TO THE RATE OF EVAPORATION OF
C          WATER.  THIS PARAMETER IS IMPORTANT IN RELATION TO F.
C          IF K/A IS GREATER THAN UNITY THEN AIR STRIPPING IS A
C          FEASIBLE TREATMENT OPERATION FOR REMOVING THE VOLATILE
C          POLLUTANTS WHOSE QUANTITY IS INDICATED BY F.  IF K/A
C          IS EQUAL TO UNITY OR LESS THAN UNITY THEN AIR STRIPPING
C          IS NOT FEASIBLE TREATMENT OPERATION DESPITE THE MAGNITUDE
C          OF F.
C*****************************************
C
C                    INPUT DATA
C
C         THESE TWELVE DATA CONSTITUTE THE NECESSARY INPUTS
C      FOR THIS PROGRAM.
C      A.  IDENTIFICATION CARD:  THE FIRST CARD IS AN IDENTIFICATION
C        SYMBOL, NAME OF SAMPLE, ETC. THAT IS PUNCHED IN THE FIRST
C        EIGHTEEN COLUMNS OF THE CARD (FORMAT: 18A4).  THIS IS ALSO
C        THE HEADING THAT IDENTIFIES AND PRECEDES THE OUTPUT RESULTS.
C      B.  CONTROL CARD:  THE SECOND CARD HAS THE NUMBER OF DATA
C        SETS TO BE RUN. (FORMAT:I3), THE GRAMS OF WATER VAPORIZED
C        DURING THE EXPERIMENT (FORMAT: F10.3), THE INITIAL GRAMS
C        OF WATER CHARGED TO THE DESORPTION APPARATUS (FORMAT: F10.3)
C        AND THE TOTAL EXPERIMENT RUN TIME IN MINUTES (FORMAT: F10.3).
C      C.  DATA CARDS:  THE THIRD AND FOLLOWING CARDS CONTAIN THE
C        CONCENTRATION, WATER, TIME DATA OBTAINED FROM SAMPLES
C        WITHDRAWN DURING THE EXPERIMENT.  THE TOTAL NUMBER OF
C        THESE DATA SETS SHOULD BE THE FIRST ENTRY IN THE CONTROL
C        CARD.  THE FIRST ENTRY IS THE CONCENTRATION DATA
C        (FORMAT: F10.3).  THE CONCENTRATION DATA CAN BE TOC, COD,
C        BOD, OC, ETC.  THE SECOND ENTRY IN EACH DATA CARD IS THE
C        WATER REMAINING IN THE DESORPTION APPARATUS (EVAPORATION
C        ACCOUNTED FOR) AT THE SAMPLE TIME (FORMAT: F10.3).  THE
C        DATA SHOULD BE PUNCHED IN CODED OF INCREASING TIME.
C
C*****************************************
      1    DIMENSION CONC(20), WATER(20), TIME(20), DAT(20), E(20), SLOPE(20)
      2    DIMENSION FI(20), CONT(20),AID(18),X(20),Y(20)
C
```

Reproduced from best available copy.

```
C          READ IN IDENTIFICATION SYMBOLS FOR SAMPLE
C
      46  READ(5,47)(AID(I),I=1,19)
      47  FORMAT(19A4)
          WRITE(6,65)(AID(I),I=1,19)
      65  FORMAT(1H1,19A4)
          READ(5,91) A, B2S ,COF,ST
      91  FORMAT(13,3F10.3)
C
C         READ IN NUMBER OF DATA SETS AND WATER LOST IN GRAMS
C         READ IN THE INITIAL GRAMS OF WATER CHARGED IN THE TOTAL TI
C
          WRITE(6,67)
      67  FORMAT(/1X'     NO C/I      GRAM H2O  MINUTES')
          DO 94 I=1,NO
C
C         READ IN AND WRITES OUT THE RAW DATA: CONCENTRATION  WATER
C              AND RUN TIME.
C
          READ(5,32) CONC(I), WATER(I), TIME(I)
          WATER(I)=COF -B2S*(TIME(I)/ST )
      94  WRITE(6,93) CONC(I), WATER(I), TIME(I)
      93  FORMAT(3F13.2)
          WRITE(6,69)
      69  FORMAT(/1X'        ITA  EXACT, NON-VOL.')
C
C         COMPUTES AND WRITES OUT EXACTIC NON-VOLATILE AND TIME
C
          DO 33 I=1,NO
          CNT(I)=WATER(I)/WATER(1)
          CON(I)=ALOG10(CNT(I))
          E(I)=(CONC(I)/CONC(1))*(CNT(I))
      33  WRITE(6,80) TIME(I),E(I)
C
C         INITIALIZES SEARCH PARAMETERS AND LINEAR REGRESSION PROCEDURE
C
      80  FORMAT(2E13.4)
          N=1
          DMAX=E(NO)
          DMIN=0.0
          GOLDUP=.618
          GOLDDN=.382
          D=GOLDUP*DMAX
          WRITE(6,59)
      60  FORMAT(/1X'EXACT, DUMMY MAX,        COV       K/1')
      59  DEN=1.0-D
          DIF2=0.0
          SLOPN=0.0
          SLOPD=0.0
C
C         COMPUTES  REGRESSION SLOPE
C
          DO 38 I=2, NO
          X(I)= CONT(I)
          EI(I)=(E(I)-D)/DEN
          Y(I)=ALOG10(EI(I))
          SLOPN=SLOPN+X(I)*Y(I)
      38  SLOPD=SLOPD+X(I)*X(I)
          AVERA=SLOPN/SLOPD
C
```

Reproduced from best available copy.

```
C          COMPUTES AND WRITES OUT STANDARD ERROR OF ESTIMATE FOR
C           X/A AND COEFFICIENT OF VARIATION FOR X/A.
C
      DO 95 I=2,N0
   95 DIF2=DIF2+ (Y(I)-AVEKA*X(I))*(Y(I)-AVEKA*X(I))
      STDA=(DIF2/(N0-2))**.5
      COV=STDA/AVEKA
      POUT=2)).-COV
      WRITE(6,71) 0, POUT, COV, AVEKA
   71 FORMAT(4E12.3)
C*****************************************************************
C
C          GOLDEN SECTION - ONE DIMENSIONAL SEARCH FOR THE ULTIMATE
C           NON-VOLATILE FRACTION IN THE SAMPLE THAT WILL
C           MINIMIZE THE COEFFICIENT OF VARIATION FOR X/A.
C
C           THE INTERVAL OF UNCERTAINTY IS REDUCED THIRTY TIMES
C           IN THE GOLDEN SECTION FASHION TO YIELD A FINAL INTERVAL
C           OF UNCERTAINTY OF LESS THAN 1.E-6 OF THE ORIGINAL INTERVAL.
C
C*****************************************************************
      N=N+1
      IF(N-21)40,11,11
   60 WRITE(6,73)
   73 FORMAT(/1X,'SOLUTION NOT FOUND,LOOSEN BRACKETING')
      DO 96 I=2, N0
   96 WRITE(6,72) X(I), Y(I)
   72 FORMAT(1X,E12.4,1X,E12.4)
      GO TO 66
   40 IF(N-2110,11,11
   10 N=N+1
      B1=POUT
      Q1=0
      Q=COV*COVMAX
      GO TO 9
   11 B2=POUT
      Q2=0
      B=B2-B1
      IF(1)2,12,1
   12 Q=(Q1+Q2)/(2.1)
      GO TO 50
    2 DQDX=Q2-Q1
      IF(DQDX)7,13,4
   13 GO TO 60
    4 QMAX=Q2
      B=B2+SQRT(ABS(QMAX-Q1))
      GO TO 50
    7 QMIN=Q2
      B=B2+SQRT(ABS(QMAX-Q1))
      GO TO 50
    1 B1=B2
      GO TO 9
    9 DQDX=Q2-Q1
      IF(DQDX)5,13,4
    5 QMIN=Q1
      Q1=Q2
      B=B2+SQRT(ABS(QMAX-Q1))
      GO TO 50
    6 QMAX=Q1
      Q1=Q2
```

```
      G=GMIN+GOLDEN*(GMAX-GMIN)
      GO TO 50
C*****************************************************************************
C
C                OUTPUT RESULTS
C
C          THE OUTPUT CONSIST OF FOUR SEPERATE SECTIONS.  THE
C      IDENTIFICATION SYMBOL IS PRINTED AT THE TOP OF THE PAGE AND
C      PRECEEDS THE NUMERICAL OUTPUT DATA.
C          1.  RAW EXPERIMENTAL DATA:  THE FIRST BLOCK OF OUTPUT
C           IS THE RAW EXPERIMENTAL DATA AS READ IN.  THE FIRST COLUMN
C           IS THE CONCENTRATION, THE SECOND IS THE GRAMS OF WATER
C           REMAINING AND COLUMN THREE IS THE RUN TIME IN MINUTES.
C          2.  NON-VOLATILE COMPUTATION:  THE SECOND BLOCK OF OUTPUT
C           IS THE FRACTION OF NON-VOLATILE ORGANIC REMAINING
C           WITH RUN TIME.  THE FIRST COLUMN IS RUN TIME IN MINUTES
C           AND THE SECOND COLUMN IS THE CORRESPONDING NON-VOLATILE
C           ORGANIC FRACTION REMAINING IN THE APPARATUS.  THIS OUTPUT
C           IS AN AID IN PLOTTING THE NON-VOLATILE RESULTS, SEE
C           EXAMPLE    .
C          3.  ULTIMATE NON-VOLATILE COMPUTATION:  THE THIRD BLOCK OF
C           OUTPUT IS THE RESULTS OF THE GRID-DIMENSIONAL SEARCH.
C           THE FINAL LINE IN THIS BLOCK OF DATA CONTAINS THE BEST
C           RESULTS.  THE TWENTY EIGHT ENTRIES ABOVE ARE THE
C           INDIVIDUAL ITERATIONS OF THE SEARCH ROUTINE.  COLUMN
C           ONE CONTAINS THE ULTIMATE NON-VOLATILE FRACTION.  COLUMN
C           TWO IS A DUMMY VARIABLE.  COLUMN THREE IS THE
C           COEFFICIENT-OF-VARIATION OF K/A.  COLUMN FOUR IS THE
C           K/A VALUE.  COLUMNS ONE AND FOUR ARE THE IMPORTANT
C           RESULTS FROM THIS BLOCK OF DATA.
C          4.  THE VOLATILE FRACTION K// PLOT:  THE FORTH BLOCK OF
C           OUTPUT IS DATA THAT AIDS IN STUDYING THE VOLATILE FRACTION.
C           THE FIRST COLUMN IS THE NATURAL LOG OF THE REMAINING
C           VOLATILE FRACTION AND THE SECOND COLUMN IS THE CHEMICAL
C           LOG OF THE REMAINING WATER FRACTION.  FIGURE    IS AN
C           EXAMPLE OF THIS DATA.  IF THE DATA PLOTS AS A STRAIGHT
C           LINE       THIS NORMALLY IMPLIES THAT THE VOLATILE
C             FRACTION CONTAINS A SINGLE VOLATILE COMPONENT (SUFFICIENT
C           CONDITION BUT NOT NECESSARY).  IF THE DATA PLOTS AS A
C           CURVED LINE THEN THE ORIGIN THIS NORMALLY IMPLIES THAT
C           THE VOLATILE FRACTION CONTAINS MORE THAN ONE VOLATILE
C           COMPONENT.
C
C*****************************************************************************
      END

*ENTRY
```

Reproduced from best available copy.

PLASTIC INDUSTRY

MG C/I	GRAM H2O	MINUTES
452.00	300.00	0.00
432.00	286.50	5.00
413.00	293.00	10.00
357.00	286.00	20.00
379.00	279.00	30.00
375.00	272.00	40.00
361.00	265.00	50.00
365.00	261.50	55.00
366.00	258.00	60.00

MIN	FRACT. NON-VOL.
0.0000	1.0000
5.0000	0.9446
10.0000	0.8924
20.0000	0.8373
30.0000	0.7769
40.0000	0.7523
50.0000	0.7055
55.0000	0.7033
60.0000	0.6964

FRACT. DIFFV	MAX.	SDV	SIA
0.430	100.000	0.035	5.634
0.204	100.004	0.038	7.691
0.533	100.004	0.033	7.542
0.556	100.007	0.033	5.701
0.636	100.000	0.032	12.150
0.656	100.007	0.033	14.557
0.615	100.007	0.033	11.126
0.663	100.001	0.032	12.547
0.660	100.000	0.033	12.556
0.635	100.003	0.033	12.631
0.641	100.000	0.033	12.[illegible]
0.642	100.000	0.033	12.[illegible]
0.643	100.000	0.033	12.[illegible]
0.643	100.000	0.033	12.[illegible]
0.643	100.000	0.033	12.534
0.643	100.000	0.032	12.541
0.643	100.000	0.033	12.544
0.643	100.000	0.032	12.545
0.643	100.000	0.032	12.546
0.643	100.000	0.032	12.546
0.643	100.000	0.032	12.546
0.643	100.000	0.032	12.547
0.643	100.000	0.032	12.547
0.643	100.000	0.032	12.547
0.643	100.000	0.032	12.547
0.643	100.000	0.032	12.547
0.643	100.000	0.032	12.547

LOG(FRAC H2O)	LOG(FRAC ORGANIC)
-0.50978-02	-0.73178-01
-0.10258-01	-0.15568 00
-0.20748-01	-0.24308 00
-0.31528-01	-0.41608 00

-0.42555-01 -0.51355 00
-0.53035-01 -0.75535 00
-0.52655-01 -0.76655 00
-0.65535-01 -0.92355 00

APPENDIX C

Hollow Fiber Device As A Desorption Apparatus

Preliminary investigative tests were performed on a device that may be an alternative to the packed column desorption apparatus. A Dow Hollow Fiber Gas Permeator was purchased. The device consists of a U-shaped bundle of hollow silicone (dimethyl silicone) rubber copolymer fibers in a 100 ml. poly-methyl-pentene beaker (Fig. C–1). This device is designed for bubble free transfer of a wide variety of common gases in gas-liquid transfer operations. Common applications include: O_2 enrichment from an air stream, oxygenation or carbonation of fermentation broth, and removal of waste gases (i.e., CO_2) from sealed environments.

The gas permeator has several characteristics that makes it attractive for desorbing gases from wastewater samples. The device is compact and can be weighed on laboratory scales to obtain water loss information. A simple apparatus is possible since a pump is not necessary for the liquid. A stirrer-bar keeps the liquid sample well mixed at all times. Figure C–2 shows the equipment arrangement employed to test the gas permeator as a gas desorption apparatus for wastewater samples.

The operating procedure employed was as follows:

1) The test solution was prepared with an approximate concentration of 1000 to 1500 parts per million of the desired volatile component in distilled water.
2) The permeator was filled with test solution (~75 ml.)
3) The permeator, with magnetic stir-bar, was weighed.
4) The permeator was set in place, and inlet and outlet air lines were connected.
5) The magnetic stirrer was activated to a reading of four to five.
6) The air was turned on and regulated to a pressure of ten to twelve psig. The rotameter was set at a constant rate of 80 on a scale of 100.
7) One milliliter samples were taken initially, after 15 minutes, 30 minutes, one hour, and at appropriate intervals thereafter (usually one or one and a half hours).
8) Finally, the permeator and contents were weighed again to find the water loss.

Three components were employed in the preliminary test on the gas permeator. Table C-1 shows the total organic carbon results for the three components tested. It is apparent from these results that this device may have limited use on gas desorption studies of wastewater. Experimental results on these three volatile components with the 46 cm. X 5 cm. raschig ring packed column allow a comparison of desorption rates between the gas permeator and a packed column (Table C-2).

It is also apparent from this data that the tube wall (40 micron) may be providing an added resistance to the transfer of the volatile species from the liquid to the gas phase. High molecular weight components may not be able to permeate the tube wall or may react or be

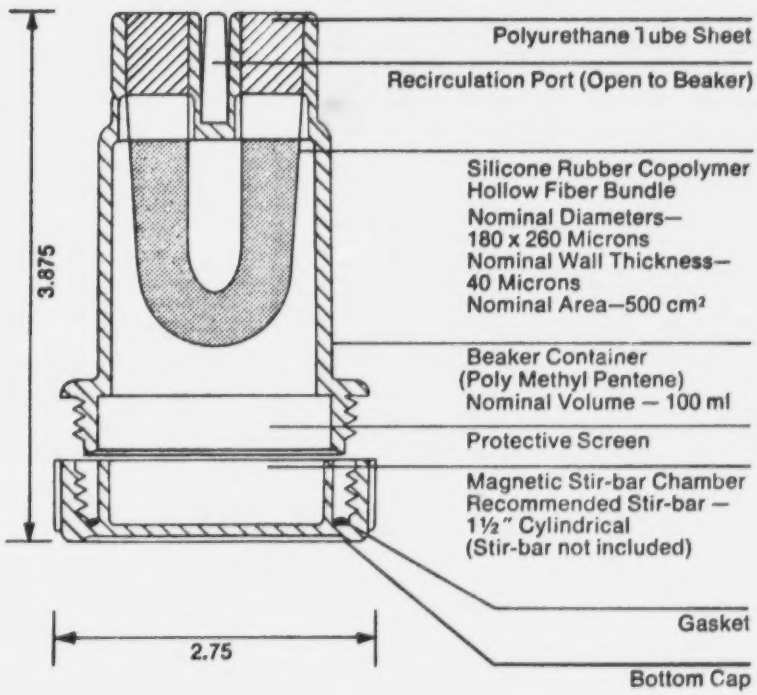


Figure C–1. The Dow hollow fiber beaker gas permeator b/HFG–1.

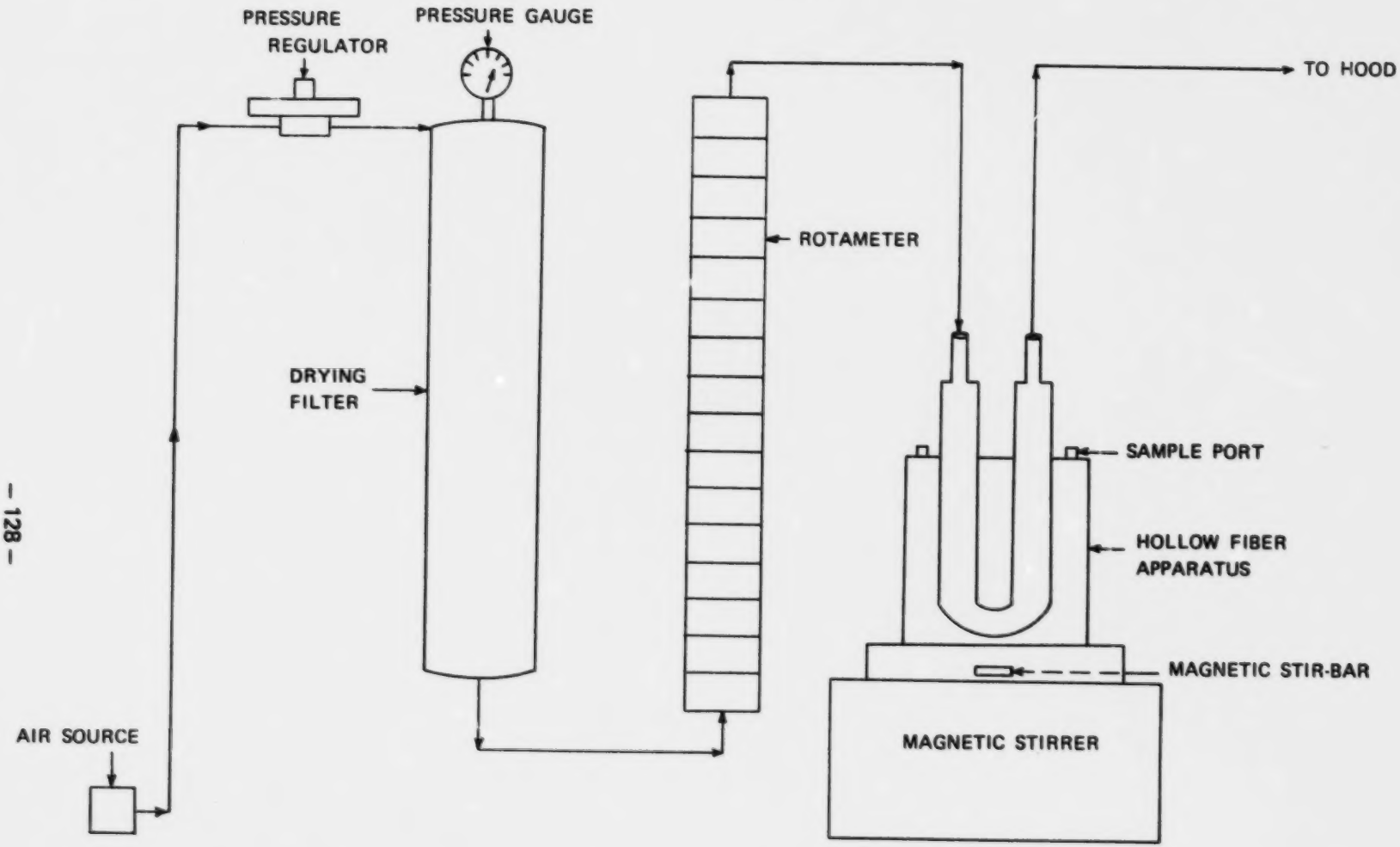


Figure C–2. Schematic diagram of equipment arrangement for gas permeator desorption experiment.

TABLE C–1

Test Results – Volatile Component Desorption in Gas Permeator

Component	Time (hrs)	Per Cent Stripped	Water Evaporated (g)
Acetaldehyde	0.0	0.0	
	0.25	47.1	
	0.5	53.2	
	1.0	57.8	
	2.0	60.7	
	3.0	85.1	---
	4.0	100.0	---
Methanol	0.0	0.0	
	0.25	11.8	
	0.5	11.8	
	1.0	12.5	
	2.0	19.0	
	3.0	22.9	
	4.0	26.9	
	5.0	32.1	
	6.5	37.4	
	8.0	46.0	19.1 rate = 2.39 cc/hr
Propanol	0.0	0.0	
	0.25	—	
	0.5	7.05	
	1.0	7.8	
	2.0	15.2	
	3.0	26.1	
	4.0	35.0	
	5.0	45.6	
	6.5	59.4	
	8.0	54.7	9.2 rate = 1.15 cc/hr

TABLE C–2

Relative Desorption Rates in 1-Hour Run Time

Component	Gas Permeator	Packed Column
acetaldehyde	57.8%	73.5%
n-propanol	7.8%	15.2%
methanol	12.5%	21.0%

absorbed by the silicone rubber copolymer. Another disadvantage is that the tube device does not simulate industrial stripping operations, as does a desorption apparatus for wastewater samples, however further detailed testing is indicated.